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INTERNATIONAL ISOCYANATE INSTITUTE, INC. CRIGINAL 119 CHERRY HILL ROAD PARSIPPANY, NEW JERSEY 07054 TELEPHONE (201) 263-7517 FAX [201] 263-8739 August 31, 1993 86930000380 SENT BY CERTIFIED MAIL TSCA Document Processing Center (TS-790) Office of Pollution Prevention & Toxics Environmental Protection Agency 401 M Street, SW; 201 East Tower Washington, D.C. 20460 Attn: 8(D) HEALTH & SAFETY STUDY REPORTING RULE (REPORTING) Dear Sir or Madam: As required by 40 CFR 716, as amended, we herewith submit a copy of the following recently completed health and safety study. Pond Study with DESMODUR 44 V20 III Project EU-ENV-101 Chemical Name CAS Number 9016-87-9 Polymeric MDI The International Isocyanate Institute (III) project identification number, has been marked as part of the title page of this report. Please refer to this III identification number in any communication regarding this study. The enclosed report does not contain any Confidential Business Information. The study is sponsored by the International Isocyanate Institute on behalf of the following: The Dow Chemical Company Miles, Inc. BASF Corporation ICI Americas, Inc. Olin Corporation Very truly yours, Managing Direc RKR/sha Enclosure

STUDY REPORT

Title

Biological effects and fate of Desmodur 44 V 20 (polymeric MDI) in artificial ponds by simulating an accidental pollution

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International Isocyanate Institute

(über Dr. Klebert)

STATEMENT OF COMPLIANCE

To the best of our knowledge and belief we declare that this study was conducted in compliance with GLP Standards (OECD, C (81) 30 (Final), May 12, 1981, published in the Bundesanzeiger on February 4, 1983; and "Grundsätze der Guten Laborpraxis (GLP)", ChemG, dated March 14, 1990, Germany).

Signatures:

Study Director:

16- 6d 1.7.93

Dr. F. Heimbach

Date

Head of Institute:

Dr. W. Pflüger

Date

CERTIFICATION OF AUTHENTICITY

Dr. F. Heimbach Title Date

Approval

Head of Institute for Environmental Biology

Dr. W. Pflüger

Title

Date

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SUMMARY

The objective of this study was to investigate effects of a simulated accidental pollution with polymeric MDI (4,4'-diphenylmethane-diisocyanate and homologues) on artificial ponds serving as aquatic model ecosystems. The artificial ponds are representative of a small standing water. Two ponds were dosed with different rates (10 and 1 g/l) and were investigated for a period of 112 days after treatment. The test substance was applied under Central European conditions in May 1992.

The test ponds used in this study are especially designed systems of 5 m³ volume which allow the establishment of identical conditions at the start of a study. The bottoms of the artificial ponds were covered with natural sediment. MDI was applied onto the sediment of the two test ponds at a rate of 10 and 1 g/l, respectively. The viscous fluid formed a more or less uniform layer on top of the sediment. In the low dosed pond the compound did not flow into the untreated section of the sediment which was separated from the treated section by a stainless steel barrier which was approximately 3 cm higher than the sediment level. In the high dosed pond some of the applied compound flowed into the untreated sediment in spite of the barrier.

Diverse aquatic communities developed spontaneously from seeds and roots of aquatic plants as well as from permanent stages of planctonic and benthic organisms. As representatives for a higher trophic level, 6 small rainbow trout were stocked separately in wire mesh cages in each pond. The cages were necessary to reduce feeding pressure on the zooplankton community. Pond-to-pond comparability was generally good.

Distribution and Fate of Polymeric MDI in Test Ponds

The applied substance was a commercial polymeric MDI product containing about 44 % 4,4'-MDI, with the balance being higher homologues and isomers. This product reacts with water to form polyureas and carbon dioxide with traces of MDA (4,4'-diphenylmethane-diamine). The polymeric reaction product formed a hardened layer at the interface between the test compound and water. Some carbon dioxide was solubilized in water, but most of the CO₂ is released as a gas forming bubbles which floated to the water surface. This activity of bubbles continuously redistributed the test substance layer on the sediment for the first weeks of the study. Small pieces were brought to the water surface, from where they sank down onto the sediment again after some time, this resulted mainly from wind and rainfall. At the same time, polymerization continued. As a result of the steady mixing and the flow of test substance in the ponds, 40 % of the applied amount was found in the untreated section of the high dosed pond at the end of the study, while only a minor fraction reached the untreated section in the low dosed pond.

The amount of MDI decreased continuously over the study period and thus the production of carbon dioxide also decreased with time. At the same time, the polymerization process protected the inner parts of the applied test substance layers from contact with water and the corresponding chemical reactions. At the end of the study, all of the applied test substance was found as hardered layers on top of the sediment in both ponds. These layers formed rather large pieces in the high dosed pond, covering about 30 % of the sediment in the treated section and 60 % in the untreated section at the end of the study. In the low dosed pond about 30 % of the treated section was covered, in the untreated section some small pieces of polymerized product could be detected. Approximately 100 % of the applied substance was recovered. The

monomer MDI or the potential reaction product MDA were not solubilized in water. The concentrations of MDA and MDI analytically determined in pond water were below the detection limit (5 - $10 \mu g/l$). Both compounds did not accumulate in fish.

Water Parameters

The production of carbon dioxide resulted in considerably lower pH in the water of the treated test ponds. The pH dropped in the treated ponds within the first days after application from approximately 9 to about pH 6.5 and pH 8 in the high and low dosed ponds, respectively. The pH was reduced in treated ponds until the end of the study, to an average 2.0 and 0.7 units lower than the control in the high and low dosed ponds, respectively. After the first days following treatment, the pH was very similar above the sediment and beneath the water surface, indicating good mixing of the pond water. The high concentration of carbon dioxide also resulted in considerably higher water hardness in pond water in treated ponds (equivalent to 80 - 100 mg CaO /l in the high dosed pond, 60 mg/l in the low dosed pond and 40 mg/l in the control pond at the end of the study). The sum of alkaline earths and the conductivity of pond water was increased accordingly.

As the high dose of MDI resulted in a higher productivity of phytoplankton and macrophytes, the oxygen concentration in the high dosed pond was higher than in the control for the last 3 months of the study (by 5 mg/l for an average); the low dose of MDI resulted in only a slight increase in oxygen concentrations of 1 - 2 mg/l for 1 to 2.5 months after application. The higher primary productivity caused even slightly lower nitrate, nitrite and ammonium concentrations in the treated ponds. Nitrate concentrations decreased drastically during the first 2 months of the study and were very low in all ponds thereafter (≤ 0.2 mg/l), indicating nitrate as the limiting nutrient for primary production. Contrary, phosphate concentrations fluctuated around 0.1 mg/l for the whole study period without recognizable differences between test ponds, characterizing a mesotrophic status of the ponds. The biological and chemical oxygen demand was not affected by either application rate of the test substance.

Biological Results

Phytoplankton communities were composed of a broad variety of species of different groups. While the communities of the control and low dosed ponds showed quite similar structures for the whole study period, some long-term effects from the high dose on the species composition of phytoplankton organisms were determined after about 2 months following application. At this time Chlorophyceae became more abundant in the high dosed pond than in the other ponds, whereas the cell numbers of the most abundant group, Cryptophyceae, decreased. On the other hand, Cryptophyceae showed slightly higher cell numbers about 1 month after application in this pond. The similarity index (Stander's Index) between high dosed and control pond is about 0.9 for the first month of the study and about 0.8 for the rest of the study, indicating only slight differences between these ponds. The similarity index is clearly higher for the low dosed pond (about 0.9; i.e., the ponds are more similar). Species diversity (Shannon-Weaver-Index of diversity and eveness of phytoplankton communities) was not affected at any time of the study. Overall, only the high dosed pond showed some slight effects from application of MDI on the phytoplankton communities which are considered as indirect effects caused by the reduced pH of the water and the physico-chemical characteristics of the water.

Zooplankton communities were composed of a broad variety of species of different organisms; the main groups were Cladocera (water fleas), Copepoda and Rotatoria (rotifers). Cladocera abundance was slightly reduced in the high dosed pond in comparison to the control 2 - 8 weeks after application. Also, Copepoda populations were slightly reduced 2 and 8 weeks after application in this pond, but an increase in population densities was observed 1 and 4 months after application. While the population dynamics of Rotatoria was similar between centrol and low dosed ponds, the high dosed pond showed distinctly higher abundances, especially 2 weeks and 4 months after application. Species diversity (Shannon-Weaver-Index of diversity and eveness of zooplankton communities) does not show any significant differences between treatments at any time of the study. The similarity index (Stander's Index) between high dosed and control pond is significantly reduced 4 weeks after application to about 0.6; the index increases thereafter to 0.9 after 2 months and decreases again to 0.8 at the end of the study. The comparison of the control and high dosed pond shows an even more reduced similarity of 0.2, 2 weeks after application. The index increases thereafter to 0.6 after 1 month and 0.9 for the rest of the study, although the Rotatoria became more abundant in the high dosed pond at this time of the study. Overall, the findings indicate some clearly expressed effects from application of MDI on the zooplankton communities 2 - 8 weeks after application in the high dosed pond, whereas the low dosed pond shows no remarkable effects. Effects are considered as indirect, caused by the reduced pH in the high dosed pond water and the altered physico-chemical characteristics of the water with subsequent changes in phytoplankton communities.

As the test substance was continuously transported onto other parts of the sediment in the high dosed pond, the benthic organisms of the "untreated" section were also severely affected. The populations of the most abundant organisms, the Oligochaeta (Tubificidae and Naididae, segmented worms), Bivalvia (mussels) and Diptera (insect larvae), were nearly extinct already 7 - 14 days after application. Organisms beneath the MDI layer starved as a result of physical obstructions or were affected by the lack of oxygen and toxic CO₂ concentrations in this microhabitat. The populations of Tubificidae, Naididae and Diptera recovered continuously thereafter and reached population densities similar to those of the other ponds approximately 2 months after application. As the generation time of Bivalvia is far too long to repopulate the sediment within the test period of this study, these organisms were not detected anymore. Contrary, the mobile Gastropoda (water snails) were not affected by the treatment. The low dose of MDI did not affect benthic organisms in the untreated section of the sediment.

The exposed fish (rainbow trout) were not affected by the application of the test substance at either rate. The abundance of Cladocera, the main natural food supply for the fish, was clearly reduced in the high dosed pond for the first weeks after application. As the fish were kept in cages they could not feed on other organisms in other parts of the pond ecosystem, e.g. insect larvae on the walls of the pend or on macrophytes. In consequence, the fish in the high dosed pond got less food than those of the other ponds, which was also very limited and which even caused some weight reduction to fish in the control. Therefore, the fish in the high dosed pond lost more weight than in the other ponds. Although some artificial fish food was added as soon as this problem was noticed, 3 fish in the high dosed pond could not recover and died 1 month after application of the test substance. They were replaced immediately by new ones. Due to the addition of fish food after the first month of the study, all fish showed a steady increase in weight and length thereafter, with no indication of differences between treatments. Overall, the exposed trout did not show any toxic symptoms or direct or indirect effects caused by the application of MDI except the temporary food shortage of the caged organisms in the high dosed pond. The lowest pH in the high dosed pond of about pH 6 did not cause lethality or apparent symptoms to fish, and all other water parameters are classified as normal.

Aquatic macrophytes (Potamogeton crispus and Zannichellia palustris, vater plants) grew better in the high dosed pond. Although their abundance was physically severely affected by the MDI layer on top of the sediment, the macrophyte biomass was clearly higher in this pond already 2 weeks after the oplication. At the end of the study, the biomass of the harvested macrophytes was 57 % nigher than in the control. In the low dosed pond 16 % more macrophytes were harvested. This increase of biomass was apparently caused by the high concentration of carbon dioxide in these ponds which enhanced macrophyte development.

In summary, neither the plied DI nor its potential reaction product MDA was detected in water or accumulated by rish. The MDI product applied to the ponds polymerized to inert polyurea on the sediment of the test ponds. This polymerization formed carbon dioxide, released as bubbles which floated to the water surface. Some carbon dioxide was solubilized in water and reduced the water pH by 2.0 units as an average in the high dosed pond (10 g/l) and 0.7 in the low dosed pond (1 g/l). This reduction and the increased macrophyte growth caused some other minor changes in the physico-chemical characteristics of the pond water. Neither application rate caused any direct effect on the pelagic community (phytoplankton, zooplankton, fish, macrophytes) of the test ponds. Some minor indirect effects caused by the production of carbon dioxide were observed in phyto- and zooplankton community structures, as well as an increase of macrophyte growth. Organisms living in the sediment (macrobenthos) were affected as a result of physical obstructions in this habitat. These populations, however, recovered to densities comparable to the control after some weeks, except for Bivalvia the generation time of which is too long to show recovery during the time period of this study.

1 AIM OF STUDY

Experiments in ponds offer the chance to test the effects of chemical substances closely simulating natural ecosystems under controlled conditions. At the same time, the distribution and fate of the chemical substances in the system can be monitored. The results can be compared to the conclusions drawn from laboratory experiments.

The objective of this study is to evestigate effects of a simulated accidential pollution with MDI on the different trophic leve (phytoplankton, zooplankton, macrobenthos, fish). At the same time the fate and distribution of the compound in the individual compartments (water body, sediment, fish) was monitored. In order to simulate the distribution on the uneven shaped bottoms of natural ponds, the bottom sediment was only partly covered by the test substance.

2 MATERIALS AND METHODS

2.1 Description of Experimental Ponds

The model ponds used are three round containers made of stainless steel which are installed next to the Institute for Environmental Biology in the Pesticide Research Center of Bayer at Monheim (geographical position: 51° 4′ N, 6° 55′ E). The diameter of the ponds is 2 m and the depth 1.8 m (Figures 1 and 2). The projected filling height amounts to 1.35 m (water only) which results in a working contents of 4.24 m³ water per pond. The pond surface is 3.14 m². The respective water level is read from a marking inside the container. The model ponds are arranged in a triangle and connected with each other by locks, 30 cm wide and 1.59 m high which provide almost identical conditions at the beginning of the test. The locks end 5 cm above the sediment in order to guarantee that they can be closed tightly despite the sediment being filled in. In each pond, a barrier made of stainless steel divide the sediment surface into two parts, each 1/2 of the total sediment surface. The barriers are inserted in a North to South direction. The barriers reach into the water for approximately 3 cm to prevent the test compound, which was added to only one of these two parts, from flowing into the other part.

The locks are closed by pressing rubber hoses fixed to the edges of the doors, by means of air pressure, against the walls of the locks. If the normal compressed-air supply (central compressed-air from the building nearby) breaks down, separate compressed-air cylinders are connected automatically.

The model ponds are dug into the ground to the upper 30 cm. In order to provide conditions as close to nature as possible, the ponds are not roofed and are exposed to outdoor weather conditions. Insects can also immigrate to the ponds.

As some of the applied test substance formed a hardened layer on part of the sediment in the treated ponds in this study, part of the sediment of the control pond was covered by stainless steel plates. Details are given in 2.5.2.

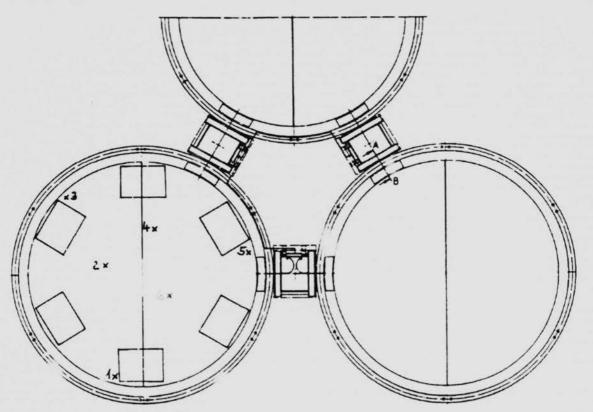


Figure 1: Top view on the 3 model ponds with indication of the sampling positions and fish cages

x = Sampling positions 1 - 6 for water, sediment and biological samples

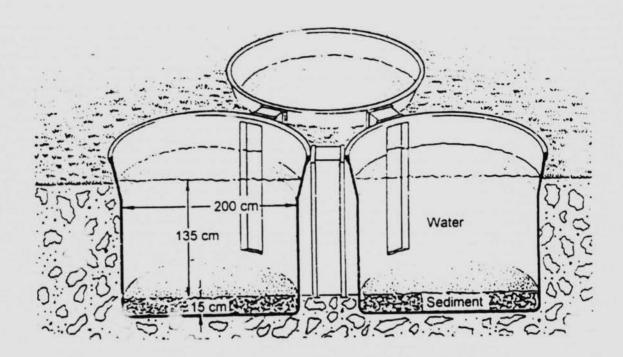


Figure 2: Schematic cross section through two model ponds (about 4.2 m³ of volume each, water depth: 1.35 m, diameter: 2 m, sediment layer: 15 cm)

2.2 Characterization of the Test Substrace

The test substance was Desmodur 44 V 20 (4,4'-diphenylmethanediisocyanate and homologues, MDI; EC-No. 615/005/01/6).

Production:

Bayer AG, PU-P Ue2

Batch-No.:

2014

Density: Viscosity: 1.24 g/cm³ 225 mPa.s

Description of the test substance:

brown, viscous liquid

Received:

02.04.1992

Solubility in water:

not soluble in water

(polymerization to inert Polyurea by separating carbon dioxide)

Characterization of the test substance according to analytical results:

0.18 % 2,2'-Diisocyanatoc phenylmethane

3.00 % 2,4'-Diisocyanatodiphenylmethane

43.60 % 4,4'-Diisocyanatod: ohenylmethane

1.30 % 3-ring-homologues to MDI

24.20 % 3-ring-homologues to MDI (isomer)

Balance

27.72 % higher homologues

According to the analytical findings,

the test substance was released until: 01.10.1992

According to analytical findings, the test substance corresponded to the specification of MDI.

Nominal doses for the study:

low dosed pond:

1 g MDI/I

high dosed pond:

10 g MDI/1

2.3 Experimental Procedure

Start of study:

May 13, 1992

End of study:

September 2, 1992

Study director:

Dr. Fred Heimbach

Technician:

Margret Gräf

2.3.1 Responsibility of Residue Analysis

Dr. Manfred Fus and Dr. Klaus Jaeger BAYER AG Central Research Department Analytical Section 51368 Leverkusen, Germany

2.3.2 Identification of Biological Samples

The identification of all biological samples was performed by experts (Biologist) at a contract laboratory:

aqua terra Institut für angewandte Ökologie e.V. Wilhelmstraße 35 A 50996 Köln Germany

The following literature was used for species identification:

Zooplankton:

FLÖSSNER (1972)
HERBST (1962)
HERBST (1976)
KIEFER (1960)
KIEFER (1978)
KOSTE (1978)
RUTTNER-KOLLISKO (1972)
STREBLE & KRAUTER (1982)

Phytoplankton:

ANAGNOSTIDIS & KOMAREK (1985)
ANAGNOSTIDIS & KOMAREK (1986)
ANAGNOSTIDIS & KOMAREK (1988)
ANAGNOSTIDIS & KOMAREK (1989)
FOTT (1971)
HEGEWALD (1982)
HEGEWALD (1988)
HUBER-PESTALOZZI (1938 - 1983)
HUSTEDT (1930)
KRAMMER (1986)
PASCHER (1983 - 1991)

The numbers of organisms were calculated according to:

SCHWOERBEL (1986) UTERMÖHL (1958)

Macrozoobenthos:

BIRO (1988)
BRINKHURST (1986)
BRYCE HOBART (1972)
CRANSTON (1982)
ELLIOT, HUMPESCH & MACAN (1988)
ELLIOT & MANN (1979)
GÖER, MEIER-BROOK & OSTERMANN (1987)
STRESEMANN (1988)

2.4 Sampling and Other Work at the Ponds

Dates and extent of sampling for residue analysis and biological examinations are given in Tables 1 - 2. Not all examinations were performed at all sampling dates.

Table 1: Dates and extent of sampling for residue analytical work

Experimental Day	Date	Water	Sediment	Fish
-1	May 12, 1992		M	
0 (before application)	May 13	M	- / ' '	
1	May 14	M		
7	May 20	M	M	
14	May 27	M	6 S	
28	June 10	M	M	
56	July 8	M	M	
112	September 2	M	M	M

M = mixed sample (water: of the whole water column, sediment: of six samples of the untreated part, fish: all fish which were exposed during the whole study period)
S = individual samples

Table 2: Dates and extent of sampling for biological examinations

Experimental Day	Date	Zooplankton	Phytoplankton	Benthos*)	Fish
- 56	March 18, '92				X
-1	May 12			6 S	X
0 (before application)	May 13	6 S	2 x 6 S		
7	May 20	6 S	2 x 6 S	6 S	X
14	May 27	6 S	2 x 6 S	6 S	X
28	June 10	6 S	2 x 6 S	6 S	X
48	June 30				X
56	July 8	6 S	2 x 6 S	6 S	X
69	July 21				X
91	August 12				X
112	September 2	6 S	2 x 6 S	6 S	X

X = the fish were weighed and measured

S = individual samples

*) 6 samples of sediment in the untreated part of the sediment

2.5 Test Procedure

2.5.1 Preparation of the Ponds

2.5.1.1 Sediment and Water

In December 1990 the model ponds were filled with sediment to a level of about 17 cm. The sediment originates from the Hönninger Weiher, a water body close to the "Oberbergisches Land". The sediment was taken there after draining the pond by means of a track-laying digger, transported in containers to Monheim and uniformly distributed among the three model ponds. The Hönninger Weiher, being about 0.1 km² in size, lies about 4.5 km North-East of Wipperfürth (Rheinisch-Bergischer Kreis) and is fed by the brook Hönninge. The pond can be characterized as oligo- to mesotrophic. It lies in a protected area and serves as a drinking water reservoir (Wupperverband).

From May 1991 to October 1991, a study with a herbicide, with a half life in water of only several days, was performed in these ponds. Two of these ponds had been treated with the herbicide, the third pond was left as control. After this study had been completed, the water and the upper layer of sediment in the treated ponds (ca. 2 cm) were discarded and the remaining sediment was transported to barrels and the ponds thoroughly cleaned. This sediment was immediately mixed, evenly distributed into all three ponds and covered with the top layer of control sediment, which had been also mixed before. After filling in the sediment, it was immediately covered with local ground water.

In addition to the passive exchange of the water via the locks, some water was pumped from one pond to the next by a small electric pump for approximately 2 months before the start of the study (until May 12, 1992).

Fifty six days before the study started (March 18, 1992), each pond was additionally inoculated with a mixed sample of different natural species of zooplankton originating from other, similar ponds located nearby the test ponds.

The sediment was characterized at the start and the end of the study. Details are given in 3.3.

2.5.1.2 Fish

On March 18, 1992 (day - 56) the ponds were stocked with 6 rainbow trout each (Oncorhynchus mykiss, RICHARDSON). The trout were obtained from a laboratory stock culture in the Institute of Environmental Biology. They were about 4 months old with a body length of about 8 cm. Exposed fish which died during the study were replaced by new ones of the same charge. These fish were kept in the laboratory during the study period; before they were inserted into the ponds they were acclimatized to physical and chemical conditions of the test ponds. In the ponds, the trout were caged to prevent predation pressure upon the zooplankton from being too high. The stainless steel cages were 20 x 30 x 42 cm in size and the mesh size was 6 mm. They were suspended in the ponds at 6 different positions (Figure 1) at a water depth of 30 to 50 cm.

Due to the exposure in cages, the fish received a decreased amount of zooplankton. In spite of periodical cleaning during the test, periphyton grew in the cages (especially in the high dosed pond), less zooplankton moved into the cages and the fish had to be fed additionally with some commercial fish food pellets about once per week ("S. I. Pellets"). Nevertheless, some fish already starved before the addition of commercial fish food started. Details are given in the results (3.4.8).

2.5.1.3 Other Activities

One day before the application of the test compound, the locks were closed and thus, the model ponds were separated from each other. The spaces in the locks between the ponds were pumped dry so that possible leaks could be recognised.

A few times during the study (see Table 10) some of the macrophytes were removed from the ponds as they might have impaired the biological sampling and also to avoid an overwhelming effect on the biocoenosis of the ponds. The dry weight of these removed plants was measured; the data are given in this report (see 3.4.9).

2.5.2 Application of the Test Substance

The test substance was added to two test ponds via a funnei through a hose directly on the sediment (nominal concentrations: 1 g/l and 10 g/l, respectively). The hoses and vessels used for the application were weighed before and after the treatment. Based on the measured gross and tare weight, the following actual applied dosages result:

Low dosed pond: 4.27 kg / pond = 101 % of nominal High dosed pond: 46.05 kg/pond = 109 % of nominal

Due to the density of the test substance, a more or less uniform layer on top of the sediment was formed by the test substance. In principle, the low dose formed a uniform layer of about 0.22 cm on top of the sediment surface in the treated part and the high dose a layer of 2.37 cm. As the sediment surface was not completely flat, the test substance was not evenly distributed on the sediment surface of the ponds. In the low dosed pond, approximately 30 % of the sediment was covered in the treated section. In the high dosed pond, some test substance reached the untreated area of the sediment by passing above or under the barrier through some holes in the sediment (although the barrier was approximately 12 cm within the sediment on average). In consequence, at the end of the study about 90 % of the treated area of the sediments surface was covered by the test substance in the high dosed pond (59 % of the final removed amount), and at least 60 % in the untreated part (41 % of the final removed amount).

To simulate the cover of part of the sediment by the MDI-layer in the treated ponds, three stainless steel plates each a segment of a circle of 45°, were put into the control pond to cover the sediment. Three eights of the total sediment was covered by these plates in the control pond. This is slightly more than the MDI-cover in the low dosed pond (approximately 15 %), but slightly less than in the high dosed pond (approximately 75 %).

2.5.3 Collection and Processing of Samples

2.5.3.1 Sampling Positions

Each pond had 6 predetermined sampling positions (Figure 1). In all ponds, the first sampling position was exactly in the South, the others followed clockwise at distances of 60° each. Numbers 1, 3 and 5 were a fixed 5 - 10 cm, and nos. 2, 4 and 6 about 50 cm away from the edge of the ponds.

Separate equipment was used for sampling each pond. The equipment was cleaned prior to consecutive sampling.

2.5.3.2 Water

The water samples for analysis were taken by means of a hose pump (Heidolph type R2R2, pump headpiece 52214 PK4). For this purpose, stainless steel tubes (diameter 9 mm) connected with the pump via silicone hoses, were dipped into the water at predetermined positions. After discarding the first half liter delivered, the water (5 l per sampling date) was pumped into brown glass bottles (2 bottles, 2.5 l each). To prevent the presence of small particles of MDI or its metabolites in the sampled water which floated on the water surface (compare 3.5.1), the water was filtered through a metal-gauze (1 mm mesh size). The samples were transported to the analytical laboratories in Leverkusen immediately after sampling (except for samples taken on day 0 (pre-treatment), which were kept cool in the darkness until day 1).

2.5.3.3 Sediment

Due to the physico-chemical characteristics of the substance (forming a viscous layer at the start of the study, and later hardened sheets on the sediment surface) it was not possible to get reproducible or analytically interpretable samples of the treated sediment. Therefore, the treated sediment was investigated for hardened substance particles with a stick on day 5 which was pressed down into the sediment by hand to get an impression of how much of the treated sediment was covered by the substance. Additionally, when the ponds were emptied at the end of the study, the thickness and amount of the hardened substance lying as lumps or sheets on the sediment surface was determined.

Sediment samples in the untreated part of the pond's were taken by means of a grab according to MILBRINK (1971) (sampled sediment surface: 23.8 m²). These imples were mixed and about 2 x 500 g were taken for analysis.

2.5.3.4 Fish

As only a small number of fish (rainbow trout, Oncorhynchus rzykiss, RICHARDSON) could be exposed to achieve a natural relationship between fish and its prey and considering the low biomass of fish, analytical examination was only performed at the end of the study. Only fish which were exposed during the whole study period were analyzed.

At certain intervals, the fish were removed from the cages, weighed and measured to investigate their health and growth. Moreover, they were regularly observed for abnormal behaviour or other symptoms of intoxication.

At the end of the study, the fish were killed ("rabbit-punch"), and later analyzed.

2.5.3.5 Zooplankton

From each pond one sample was taken at each of the six sampling positions. The samples were individually fixed in 70% ethanol. The sampling was done with a commercial water-proof vacuum cleaner (Fa. Elektrostar, Starmix Zyklon HG 81). The 120 cm long suction tube (diameter 5 cm) was immersed vertically from the water surface down to about 25 cm above the sediment and pulled out again within about 3 seconds. During this time, approximately 7 l of water was pumped, 5 l of which were filtered through a plankton screen of Fa. Kosmos (mesh size 56 µm).

For the species determination, the zooplankton samples were preserved in glycerine and observed under a binocular or a transmission light microscope.

The biological evaluation of the zooplankton, phytoplankton and benthos samples was performed according to GLP-regulations by "aqua terra" (see 2.3.2).

The samples were evaluated microscopically in the laboratory by determining and counting the individual organisms. As most of the samples showed a very high density of organisms, they were diluted for counting and three or six sub-samples were evaluated under a binocular. The larger zooplankters (> 1 mm) were counted in the undiluted sample. Not all organisms were determined to the species level, only the most abundant species and/or those which were fairly readily determinable were identified to this level.

2.5.3.6 Phytoplankton

The phytoplankton samples were obtained from the same water samples as the zooplankton samples. Six individual unfiltered samples (about 1 l) were mixed with Lugol's solution, additionally about 90 ml per unfiltered sample were fixed with formaldehyde (resulting in a 4 % formaldehyde solution).

For evaluation of these samples by "aqua terra" (2.3.2), 50 ml of the thoroughly shaken phytoplankton sample were later emptied into a sedimentation chamber for phytoplankton in the laboratory and allowed to stand for several hours. The determination and counting of the cells were made by means of a reversed microscope. Depending upon the concentration of algae, the number of fields to count were chosen.

2.5.3.7 Macrobenthos

Six samples of sediment of the untreated part were taken by means of a grab according to MILBRINK (1971) (sample size approximately 23.8 cm²). The samples were individually screened through a metal screen of 500 μ m mesh size and the residue was fixed with 5% formaldehyde. Later, the organisms were selected from the preserved samples which were used for species identification and enumeration by "aqua terra" (2.3.2). As some part of the test

compound also reached the untreated part of the sediment in the high dosed pond, the samples in this pond contained a high amount of the test substance. This amount differed from sample to sample drastically. As an average, a content of 50 % test substance in each screened sample should be considered.

2.6 Determination of the Physico-Chemical Water Parameters

In order to determine the physico-chemical parameters and the chlorophyll content of the water, a mixed sample of the whole water column was taken by means of a water ladle (approximately 2.0 l).

The following parameters were determined at an approximate 14 day interval: turbidity, conductivity, ammonium, nitrite, nitrate, phosphate, carbonate hardness and sum of alkaline earths. Also, about every 2 weeks the COD (chemical oxygen demand), the BOD (biological oxygen demand) and the chlorophyll and phaeophytin content were determined.

Carbonate hardness and sum of alkaline earths were determined by means of the Aquamerck Water Laboratory (Merck). For determination of conductivity, the measuring device LF 56 with the measuring electrode LTA 100/k of the Fa. WTW (WISSENSCHAFTLICH-TECHNISCHE WERKSTÄTTEN, Weilheim, Germany) was used. Conductivity is expressed in μ S/cm (= μ mhoS/cm). The BOD was determined over a period of 5 days with a BOD measuring device (WTW, BSB 600). The other parameters were determined by means of commercial photometric tests (WTW). Determination of chlorophyll a and phaeophytin (a metabolite of chlorophyll) was made in accordance with Nusch (DIN 3842 L 16 (DEV 1987)). For this purpose, Whatman GF/C glass fibre filters with a pore size of 1 μ m were used. During the 24 hour extraction period the samples were agitated. The final extinction measurement was made in a 1-ray photometer (type MPM 1500 of WTW) at a wavelength of 665 nm.

During the first days after application, oxygen content, pH and temperature were measured two to three times a day and thereafter several times per week at about 15 cm from the edge of the pond and 20 cm and 100 cm below the water surface. An electronic measuring instrument for the measurement of oxygen of Fa. WTW was used (Oxi 191, electrode EOT 190 suitable for greater water depths, battery-driven stirrer BR 190). Simultaneous with the oxygen content determinations, the pH-value and temperature were determined (pH-meter of Fa. WTW (pH 196 T) with armature TA-pH/T suitable for greater water depths). From day 2 to day 42 these parameters were measured above the treated and untreated sediment, and thereafter only one measurement in the area between these parts was taken.

2.7 Assessment of the Biomass of the Macrophytes

Several times during the study some of the macrophytes were removed by cutting off the plants near the sediment. As the macrophytes floated to the water surface, they were collected and their dry weight determined (see Table 10). This kind of sampling allows only a semi-quantitative comparison of the three ponds, but no quantitative statement on macrophyte density. At the end of the study, when the ponds were emptied, macrophytes were removed by hand from the sediment (some of them with roots) and dried before their biomass was determined by weighing.

2.8 Similaritity and Diversity Indices

Statistical evaluation of the study data was performed by statistical exp τs at the Technical University of Aachen (see appendix IV for details):

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Two different types of indices were used to compare the plankton community structure in the artificial ponds: The "Shannon-Weaver-Diversity", a well established and frequently used index (WASHINGTON 1984) calculated from the zooplankton and phytoplankton data; and, a randomized similarity analysis based on Stander's Similarity Index (JOHNSON & MILLIE 1982, SMITH et al 1986) using the relative abundances of single species in the zooplankton and phytoplankton communities. Stander's Similarity index provides information on the degree of similarity of the zooplankton communities in ponds to be compared to each other. It is a randomized non-parametric test. In the case of the three test ponds, a set of (3 x 6) 18 samples from a sampling date provided sufficient data for this test (ENGELS & RATTE 1992). For every possible pairing of samples, the Stander's Index of similarity is calculated giving a "Within-Similarity (W)" for samples from the same pond and a "Between-Similarity (B)" for samples from different ponds. If the zooplankton communities of two samples compared are identical, the value obtained is 1, in any other case the value will be lower than 1. The relation of the mean "Between-Similarities (B)" to the mean "Within-Similarities (W)" is called "Lvalue", and provides a measure of similarity between two ponds. Using a statistical procedure proposed by SMITH & MERCANTE (1989), confidence limits of the "L-value" can be calculated for each pair of ponds. L-values equal to 1 indicate communities in two ponds are identical.

2.9 Analysis

The analysis of all analytical samples (water, sediment and fish) was performed according to GLP-regulations in analytical laboratories (see 2.3.1). The results are given as an appendix to this report.

2.10 Filing

All the raw data and the original of the report belonging to this study are filed in the GLP-archive of the Crop Protection Research Division (BAYER AG, Pflanzenschutzzentrum Monheim, building 6500). A reserve sample of the test substance is stored in the archives of Bayer AG, Central Research Department, Analytical Section (OAL), "GLP-Probenlager", building O 13, 51368 Leverkusen, Germany.

3 RESULTS AND DISCUSSION

3.1 General Conditions and Meteorology

3.1.1 Meteorological Conditions

As the development of an aquatic system depends to a high degree on climatic parameters, records of mean daily air temperature, sunshine duration, wind speed and precipitation at the nearby experimental farm Laacherhof of the Bayer AG were used to characterize climatic conditions in 1992 (Figures 3 and 4, Table 3).

The application was performed on May 13, 1992. The data of the first eight days after the application are summarized in Table 3. The average air temperature in May was 15.9 °C, which is 2.6 °C higher than the previous 26 year mean. There was 45 % less precipitation (35 mm) and 37 % more sunshine (252 hours) than normal. In June, the average temperature (17.7 °C) was only slightly higher compared to the previous 26 year mean (16.0 °C), precipitation (105 mm) was higher (31 %), and 28 % longer sunshine duration (200 hours) than normal was recorded. Also in July, the temperature (19.4 °C) was higher than normal by 1.2 °C, the amount of precipitation (66 mm) was approximately 10 % lower and there was 29 % more sunshine (232 hours) than normal. In August, the mean temperature (19.7 °C) was 1.7 °C higher than usual, the sunshine duration (183 hours) was similar to the previous 26 year mean and the precipitation rate (104 mm) was notably higher than usual (52 %). Mean temperatures in September (15.1 °C) were similar to the 26 year mean, precipitation (49 mm) was 13 % lower than normal, and sunshine duration (155 hours) was 22 % longer than normal.

Generally, the climate was distinctly warmer and slightly dryer in the year 1992 than the previous two decades.

Table 3: Climatic conditions during and shortly after application (average values)

Date	Experimental Day	Temperature (°C)	Sunshine Duration (h)	Speed of Wind (m/sec)	Precipation (mm)
13.05.92	0	15.1	11.5	1.1	0
14.05.92	1	22.4	12.8	2.6	0
15.05.92	2	24.0	13.3	1.3	0
16.05.92	3	17.4	12.8	3.0	0
17.05.92	4	12.5	9.3	1.8	0
05.92	5	16.8	11.5	1.8	0.2
19.05.92	6	18.5	13.5	3.0	0
20.05.92	7	18.9	13.3	2.3	0
21.05.92	8	18.9	12.8	1.0	C

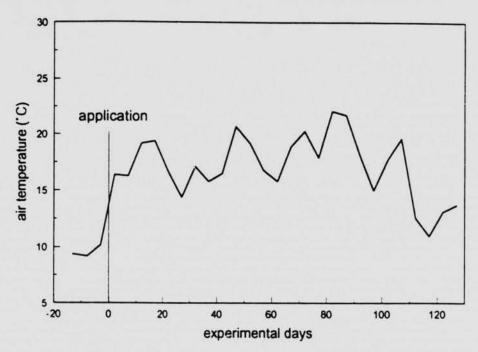


Figure 3: Air temperature fluctuations during the study period recorded at a nearby experimental farm. Plotted values are means calculated for a five day period (pentad).

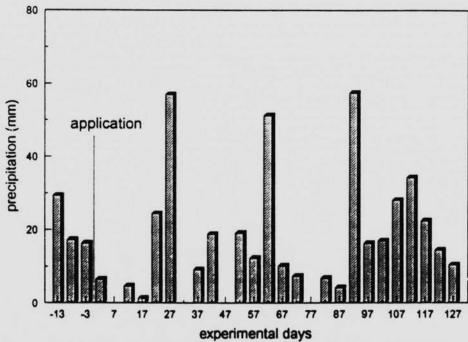


Figure 4: Amount of precipitation during the study period recorded at a nearby experimental farm. Each value represents total precipitation of a five day period (pentad).

3.1.2 Water Levels in the Artificial Ponds

The water levels in the ponds varied during the test period due to rainfall or evaporation (Table 4). The trends were the same in the different ponds.

Table 4: Water level in test ponds (deviation from zero-leve. in cm)

Experimental Day	Control pond	Low dosed pond (1 1)	High dosed pond (1) g/l)	
0	0	0		
2	- 0.5	- 0.5	-05	
5	- 2.0	- 2.0	- 2.0	
8	- 4.0	- 4.0	- 4.0	
9	- 4.0	- 4.0	- 4.0	
12	- 4.0	- 4.0	- 4.0	
16	- 8.0	- 9.0	- 7.0	
20	- 6.0	- 7.5	- 7.0	
22	- 5.0	- 7.0	- 6.0	
27	0	- 1.0	0	
30	- 1.5	- 3.0	- 1.5	
33	- 2.5	- 4.0	- 3.0	
37	- 4.0	- 6.0	- 5.0	
47	- 6.0	- 8.0	- 6.0	
51	-7.0	- 8.0	- 7 .0	
57	- 8.0	- 9.5	- 8.0	
70	- 8.0	- 9.0	- 8.5	
79	- 10.5	- 11.5	- 11.0	
84	- 12.0	- 13.0	- 11.5	
89	- 13.0	- 14.0	- 13.0	
104	- 11.0	- 12.0	- 11.0	
112	- 9.0	- 10.0	- 9.0	

3.2 Physico-chemical Water Parameters

3.2.1 Temperature

The temperature curves for the individual positions and ponds are presented in Figures 5 and 6. Shortly after treatment, the water temperature near the surface increased from 12 to about 18° C (day 3), during the remaining study it fluctuated between 18 and 23°C due to changing weather conditions. Near the sediment surface the temperature increased, after a short delay, from 12°C to 17°C, and showed distinct fluctuations during the test period from 17°C to 23°C. Until approximately day 30, the temperature curves above the sediment indicated that during short periods of high subsurface temperature, a gradient of up to 4°C existed between the water surface and sediment surface. However, these differences existed only for short periods and stable temperature stratification in the water column was not detected. In general, there was no temperature difference between the three pond aring the entire study period.

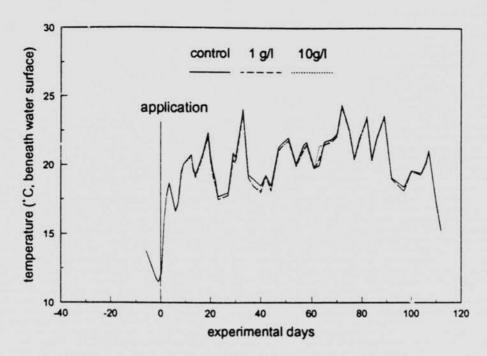


Figure 5: Water temperature in the artificial ponds beneath the water surface (at a water depth of approximately 20 cm)

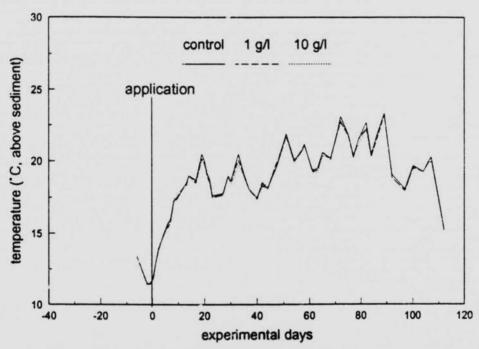


Figure 6: Water temperature in the artificial ponds above the sediment (at a water depth of approximately 100 cm)

3.2.2 Oxygen Concentration

The oxygen concentrations (Figures 7 and 8) varied between 9 and 22 mg/l. These values indicate high productivity of the phytoplankton and macrophytes which result in concentrations well above the oxygen saturation at these temperatures (8.4 - 9.2 mg/l). The relatively intense sunshine during the study period certainly contributed to this activity. During the pretreatment period and up to approximately day 25, the oxygen concentration in all test ponds corresponded very well. Thereafter, the oxygen concentrations in the treated ponds were higher than those in the control pond. In the low dosed pond, these difference became smaller after approximately day 60, and the oxygen concentrations of both ponds were similar at the end of the study. In contrast, oxygen concentrations in the high dosed pond were notably higher (by 5.0 mg/l for an average after day 27) until the end of the study. This difference was caused by the high density of macrophytes in this pond (see 3.4.9).

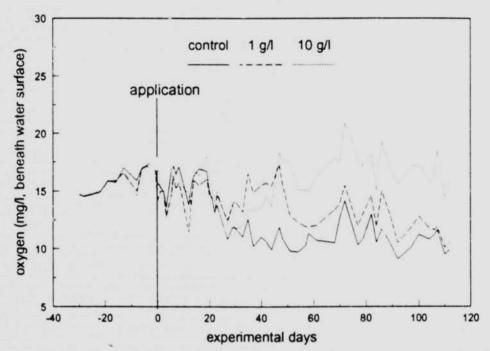


Figure 7: Variations of oxygen concentration in the artificial ponds approximately 20 cm beneath the water surface

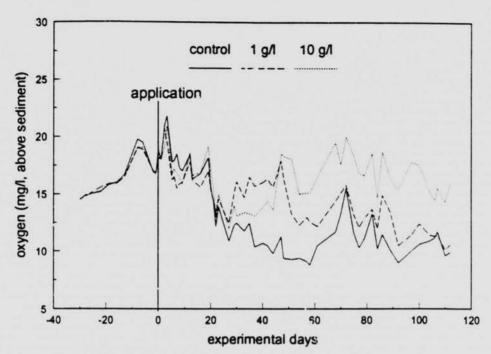


Figure 8: Variations of oxygen concentration in the artificial ponds above the sediment (at a water depth of approximately 100 cm)

During the first days of the study, oxygen concentration was measured several times per day (Table 5). The data indicate a slight increase of oxygen concentration in the water during the daytime which was caused by the photosynthetic activity of the primary producers. As this activity depends on the weather conditions (especially temperature and sunshine intensity), the increase differs from day to day. Maximum oxygen concentrations were recorded about noon. Due to the reduced productivity during night time, oxygen concentrations were distinctly lower the following morning. This trend is slightly more distinct in the deeper water than near 'e water surface. These trends were generally the same in all three ponds.

Table 5: Daily development of oxygen concentrations (above the treated sediment)

			oxygen concentrations (mg/l)					
Experi- mental Day	Time	beneath surface	above sediment	low dosed (1 g/l) beneath surface	above sediment	high dose (10 g/l) beneath surface	d pond above sediment	
2	08:20	12.2	20.1	11.4	18.7	13.1	17.9	
2	11:45	14.9	20.9	15.0	20.7	14.1	19.2	
2	16:10	13.8	23.5	12.9	20.1	12.4	21.3	
5	08:15	16.7	17.3	15.1	15.3	15.4	16.1	
5	11:45	16.9	17.8	14.7	16.2	14.8	16.7	
5	16:15	15.2	19.9	12.8	19.2	13.0	20.2	
6	08:20	17.3	17.9	16.3	16.6	17.1	17.2	
6	16:40	17.1	19.0	14.7	18.5	15.5	20.1	
7	07:45	16.4	18.5	15.2	15.5	16.6	16.8	
7	16:20	16.2	20.6	16.1	19.2	16.6	19.6	
8	08:15 16:30	17.1 15.1	17.3 18.9	15.7 13.9	15.9 16.5	16.4 15.2	16.5 17.4	
9	08:15	16.4	17.0	15.0	16.0	15.6	15.9	
9	16:20	14.8	18.7	13.5	16.6	13.4	17.2	
13	08:15	15.6	16.3	14.5	16.2	13.7	16.6	
13	16:15	14.5	17.4	14.7	17.4	13.8	19.3	
14	08:15	16.3	16.5	15.9	16.0	16.8	16.8	
14	17:00	17.7	19.2	16.7	18.0	17.3	19.5	
16	08:15	16.9	16.8	15.5	15.6	16.3	16.8	
16	16:00	16.2	18.5	15.2	17.4	16.2	18.8	

3.2.3 pH

Figure 9 and 10 snow the pH values during the pretreatment period and the study period, measured until day 42 at two different water depths above the region of sediment where the MDI was applied. Thereafter, pH was measured in the center of the ponds (i.e. in the area between the untreated and treated sediment). The results clearly show dose related pH differences caused by the application of MDI. The pH of all three ponds corresponded very well up to day 2. Then the pH of the high dosed pond above the sediment declined rapidly within a few hours from pH 8.64 at 11:45 (day 2) to pH 7.82 (day 2) at 16:10 and pH 6.39 on day 5 (at 11:45). After a slight delay, the pH beneath the water surface declined to 7.55 on day 5. During the remaining study period the pH dropped to a pH between 6.0 and 6.5 above the sediment (with a minimum value of pH 5.7 on day 20, Figure 13) and to pH 6.5 - 7.0 near the water surface. In the final period of the study the pH increased again to approximately pH 7.1 in the high dosed pond, which was still distinctly lower than the pH in the control pond (pH 8.7). Overall, the pH of the high dosed pond was approximately 2.0 units (after day 2) lower on average than in the control pond. The greatest difference between control and high dosed pond was recorded on day 12 (3.5 units).

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The pH of the low dosed pond was slightly lower than in the control pond for the whole study. Just a very few records show similar pH values in these two ponds. The greatest difference was measured on day 6 (1.4 units). This difference, however, was quite low, and on average after day 2 the pH in the low dosed pond was only 0.7 units lower than in the control pond.

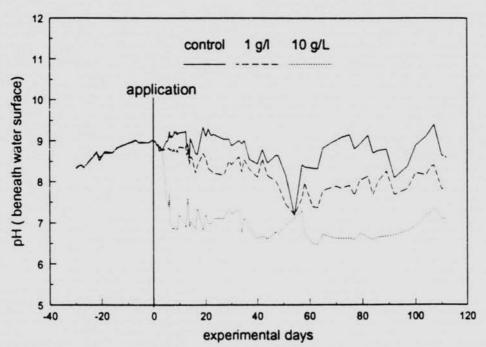


Figure 9: Fluctuations of pH in the water beneath the water surface

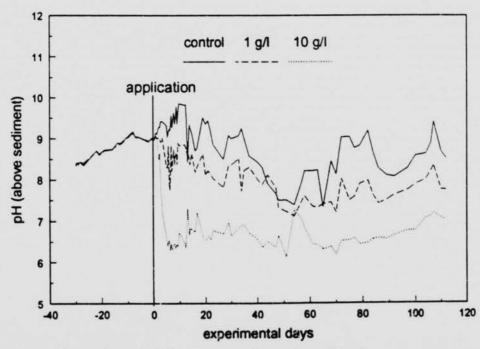


Figure 10: Fluctuations of pH in the water above the sediment

With the exception of a very few records, the pH values were very similar above the sediment and below the water surface, indicating good mixing of the pond water. This was caused by the production of CO₂-bubbles from the applied MDI (see below) and by the natural exchange between water and air (e.g. as a result of wind).

The pH was recorded at different locations in each pond during the first weeks after application. It was recorded above that part of the sediment which was treated with MDI as well as above the untreated part. The results are given in Figures 11 - 13. The data do not show any significant differences better these locations, indicating thorough mixing of the pond water (as discussed above).

The development of different pH trends in the three test ponds was caused by the fate of MDI in the treated ponds (see 3.5.1). During the polymerization of MDI at the water/MDI interface, carbon dioxide was produced. While some of the CO₂ formed bubbles which floated to the water surface, some was also solubilized in the water which increased the carbon acid concentration and resulted in a decline of the water pH.

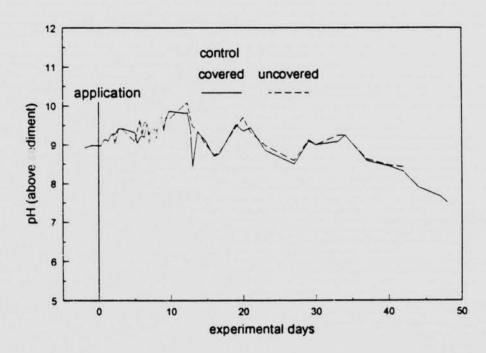


Figure 11: Comparison of water pH in the control pond above the covered and uncovered part of . .: sediment

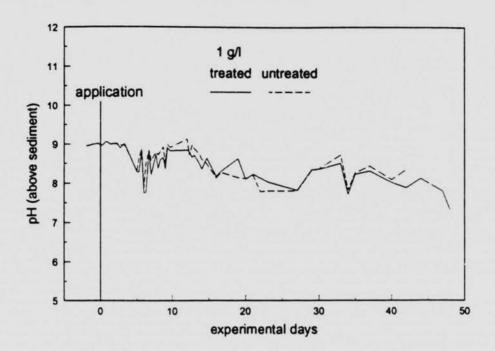


Figure 12: Comparison of water pH in the low dosed pond above the treated and untreated part of the sediment

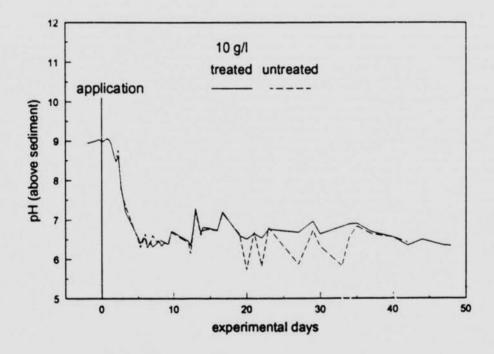


Figure 13: Comparison of water pH in the high dosed pond above the treated and the untreated part of the sediment

3.2.4 Ammonium, Nitrite and Nitrate

Nitrate is an important nutrient for phytoplankton and macrophyte growth. Under the aerobic conditions in this study, it was produced from ammonium and nitrite (ammonium \rightarrow nitrite \rightarrow nitrat). On the other hand, it was used by primary producers to build biomass.

Ammonium concentrations (Figure 14) were low. They ranged between 0.02 to 0.39 mg/l in all ponds. Until day 42 the concentrations showed similar fluctuations in all ponds (0.02 to 0.08 mg/l). Thereafter, slight differences between the ponds were observed. While ammonium concentrations in the high dosed pond remained within this range (0.05 mg/l), the concentrations in the low dosed and control pond increased to approximately 0.1 mg/l (low dosed pond) and 0.15 mg/l (control pond) with a maximum of 0.39 mg/l in the control pond on day 55.

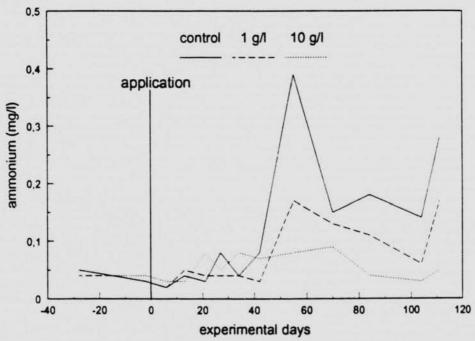


Figure 14: Ammonium concentrations in the test ponds

Nitrite concentrations (Figure 15) ranged between 0.007 and 0.149 mg/l in all three ponds. Until day 21, nitrite concentrations of the 3 ponds corresponded well. Thereafter, the concentrations in the high dosed pond decreased to the lowest measured value (0.007 mg/l on day 111). In the low dosed pond the concentrations remained relatively constant, and in the control pond the concentrations increased slightly to a maximum concentration of 0.149 mg/l on day 111.

Nitrate concentrations (Figure 16) varied between 0.03 and 5.1 mg/l. Throughout the study the concentrations of nitrate in all three ponds decreased from approximately 5 mg/l (day -28) to approximately 0.1 mg/l. This decline was caused by the production of organic material by the primary producers which use nitrate as a nutrient. Under local climatic conditions, this production begins each year in April. The increasing number of phytoplankton cells from days

0 to 20 (3.4.2) and increasing macrophyte growth (3.4.9) demonstrates this turnover of nutrients. After day 42, slight differences between the test ponds were recorded which indicate slightly higher productivity in the high dosed pond (i.e. lower nitrate concentrations in water) than in the control pond. Also the low dosed pond showed slightly lower nitrate concentrations than the control pond.

The dose relationship to nitrate concentrations resulted in slight differences in ammonium and nitrite concentrations in the test ponds. Additionally, oxygen concentration was higher in treated ponds than in the control pond favouring nitrate formation which resulted in lower ammonium and nitrite concentrations in the treated ponds, especially the high dosed one. The results also show that natural nitrification was not disturbed by the test substance.

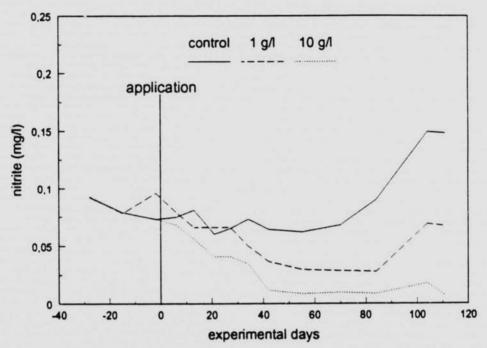


Figure 15: Nitrite concentrations in the test ponds

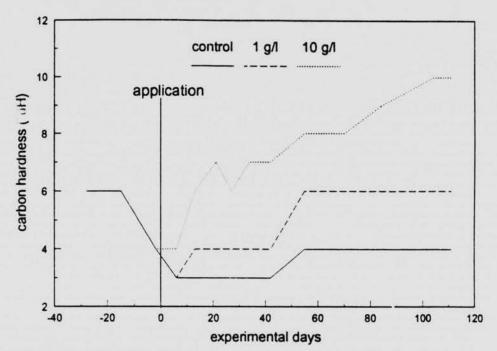


Figure 17: Carbon hardness in the test ponds (1 odH = 10 mg CaO /1)

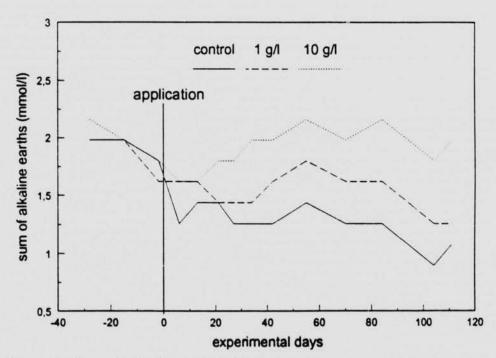


Figure 18: Sum of alkaline earths in the test ponds

The water conductivity in the treated ponds increased by hydrolysis of calcium bicarbonate and other salts (Figure 19). Thus, carbon hardness, alkaline earths and conductivity increased in the treated ponds due to the dose dependent increase of carbon dioxide in water.

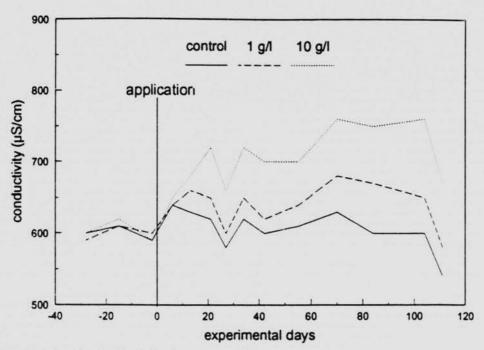


Figure 19: Conductivity in the test ponds

3.2.6 Phosphate

Phosphate concentrations were determined until day 42 by a photometric test which allowed only a rough estimation within the concentration range of this study (Figure 20). Thereafter, a more suitable photometric test was used. The results show only negligible differences between control and treated ponds which cannot be attributed to the application of MDI. The concentrations indicate a mesotrophic status of the test ponds.

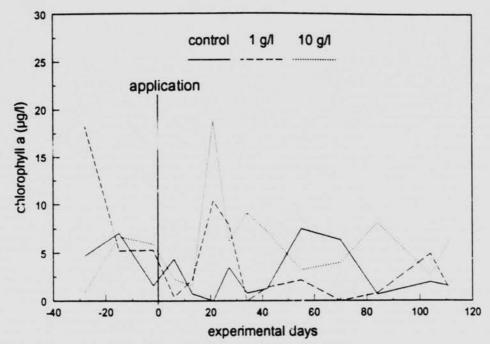


Figure 21: Chlorophyll a concentrations in the test ponds

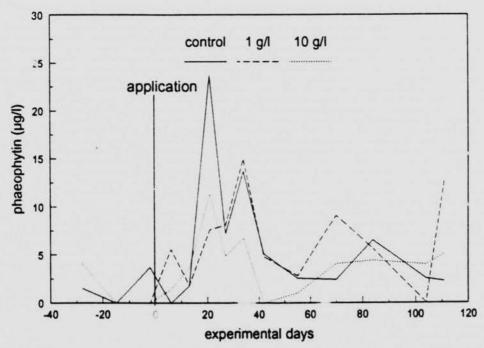


Figure 22: Phaeophatin concentrations in the test ponds

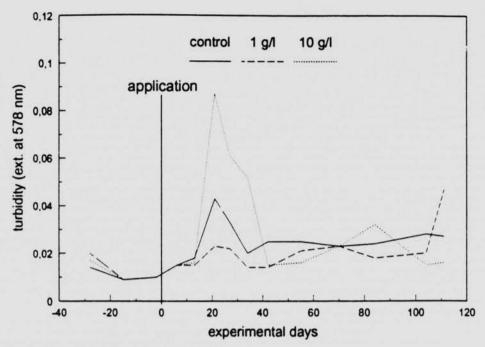


Figure 23: Turbidity in the test ponds

3.2.8 Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD)

The results of Figure 24 show that the COD fluctuated from 12 to approximately 30 mg/l in all ponds throughout the study period. This corresponds to a natural COD range for ponds of this kind and no dose related effects were recognizable.

The BOD (Figure 25) was determind after a five day exposure period under constant laboratory conditions (constant darkness, 20 °C). As with previous studies conducted in these test ponds, the BOD was low (less or equal 5 mg/l). This range can also be considered natural for these ponds. Only one distinctly higher concentration was measured on day 27 in all ponds. This may be due to a greater amount of organic particles in the water, as the recorded turbidity on day 21 is clearly elevated (Fig. 23). On the other hand, as there is a 6-day gap between these two findings and the BOD was not determined on day 21, no further explanation for this peak of BOD on day 27 can be given.

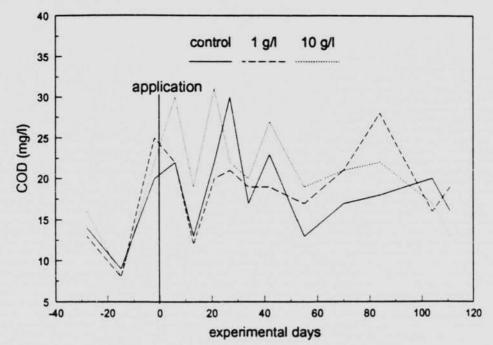


Figure 24: COD (chemical oxygen demand) in the test ponds

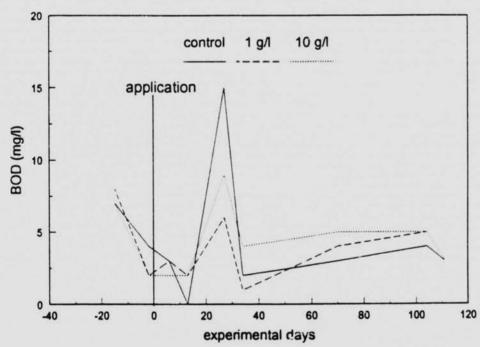


Figure 25: BOD (biological oxygen demand) in the test ponds

3.3 Characterization of the Sediment

The sediment was analysed for the parameters listed in Table 6 at the start and end of the study. The investigation was performed in the Institute of Environmental Biology and in a public research institute nearby (Landwirtschaftliche Untersuchungs- und Forschungsanstalt, 5300 Bonn, Germany) using broadly accepted methods. At the start of the study, prior to treatment a sample composed of sediment from all three ponds was analyzed; and, at the end of the study, the untreated part of the sediment of each pond was collected and individually analyzed. Additionally, individual samples from each pond were analyzed for microbial activity. This analysis was also performed by measuring the production of microbial carbon dioxide in the samples at the end of the study.

The exchange of biomass during the vegetation period (May to September) is believed to have caused the slight increase in sediment pH in the control pond. Based on the water pH findings, the sediment pH in the treated ponds was dose related lower compared to the control sediment. The decrease in pH was caused by the greater amount of CO₂ in treated ponds (see 3.2.3). No substantial differences in phosphate (P₂O₅) or potassium (K) content were recognized at the start of the study or between the ponds. Other basic ions (Na, Mg, and Ca), however, increased slightly in concentration compared to the initial value in the control pond. The concentrations in the treated ponds were considerably lower, especially in the high dosed pond. The reason for the differences compared to the control sediment result from the different water chemical characteristics. In the treated ponds more ions were dissolved from the sediment resulting in a higher concentration of alkaline earths (3.2.5).

The cation exchange capacity confirms other results in the study. The "T-value" is the potential maximum quantity of cations which can be retained and released from the sediment, the "S-value" is the sum of exchangeable basic ions (Ca-, Mg-, K- and Na-ions) and the "V-value" is the percentage factor of the basic ions at the "T-value". As the concentration of basic ions in the sediment of the treated ponds was lower than in control sediment, the "S-value" and "V-value" were lower compared to the control.

According to the regulation DIN (1973), the particle size distribution of the sediment in this study is characterized as "silty sand".

Microbial activity slightly increased in the control pond during the study, due to the exchange of biomass during the vegetation period. In the treated ponds, this increase was less pronounced, but is not considered to be caused by MDI because the high dosed pond demonstrated greater microbial activity than the low dosed pond. The data, however, must be interpreted with care, as only a very few samples were investigated. On the other hand, the data allow a rough characterization of the sediment status.

The data from the C- and N-content analyses must also be interpreted with care. While the C-content data do not show any dose related differences between treatments (except a slight increase at the end of the study in comparison to the start of the study), the N-content was slightly higher at the end of the study in the high dosed sediment. Although the concentration difference between the ponds is small, it may have been caused by the presence of test substance or hydrolysis products in the sediment samples, even at the end of the study.

Table 6: Characterization of sediment at the start and end of the study

Parameter		Start of Study	End of Study			
			Control	Pond 1 g/l	Pond 10 g/l	
pH		5.9	6.5	6.1	5.9	
P ₂ O ₅ (mg	/100g)	16	17	17	16	
Na (mval)		0.26	0.42	0.32	0.33	
Mg (mval)		0.44	0.56	0.55	0.49	
Ca (mval)		5.12	6.17	5.33	5.06	
K (mval)		0.09	0.10	0.10	0.10	
Cation Exchange Capacity	S-value T-value V-value	5.91 11.53 51.26	7.25 10.0 72.8	6.28 9.98 63.0	5.97 9.68 61.6	
C-content (%)		2.28	2.85	2.50	2.65	
N-content (%)		0.12	0.08	0.12	0.15	
Particle size distribution (weight %)		52.6 44.8 2.5	n.a. n.a. n.a.	n.a. n.a. n.a.	n.a. n.a. n.a.	
Microbial Activity (mg CO ₂ /h*kg sed.)		day -1 day 112	18 57	20 31	19 40	

n.a. = not analyzed

3.4 Biological Results

3.4.1 Observations during Application

No acute et is from the MDI treatment were observed on fish, water fleas or other invertebrates during the first days after treatment in each pond. Also, the carbon dioxide gas bubbles floating from the sediment to the water surface did not seem to harm any of these organisms.

3.4.2 Phytoplankton

Phytoplankton density ranged between 80 to 800 cells/ml. Density fluctuations show the same tendency in all three ponds (Figure 26). After a peak on day 14 (control and low dosed pond) and day 28 (high dosed pond), the algae density decreased to 80 - 170 cells/ml on day 112. The highest density was determined in the low dosed pond (808 cells/ml on day 14), while peaks in the control (day 14) and high dosed pond (day 28) were similar at about 600 cells/ml. This shows that the treatment did not affect the sum of algae cells in comparison to the control with the exception of slightly higher celi numbers in the treated ponds for the period of approximately day 20 - 40. Nevertheless, a slight dose dependent increase in cell numbers of Cryphtophyceae on day 28 could be interpreted in all three ponds (Figure 27). However, at the next sampling, on day 56, the high dosed pond demonstrated a distinctly lower number of Cryphtophyceae and a distinctly greater number of Chlorophyceae (Figure 29) in comparison to the control and low dosed pond.

Comparison of the curves plotted in Figure 27, 28 and 29 shows that generally species of the orders Cryptophyceae and Conjugatophyceae comprised a major fraction of the phytoplankton community in the ponds. While these two groups developed similarly in the control and low dosed pond, this same trend was not observed in the high dosed pond (as already indicated). In this pond the Crypthophyceae population decreased until day 56, at the same time at which a peak was observed in the other two ponds. The population of the Chlorophyceae increased to a maximum of about 100 cells/ml in the high dosed pond also at this same time, while in the other two ponds cells of this organisms group were basically not existent (Figure 29).

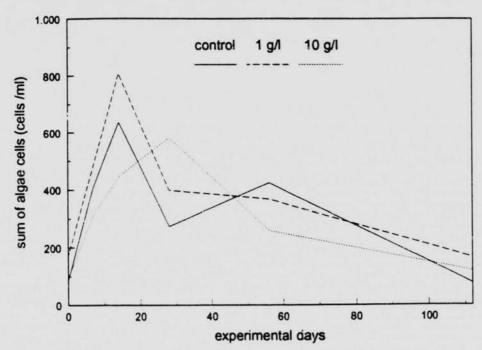


Figure 26: Fluctuations of phytoplankton density in the test ponds

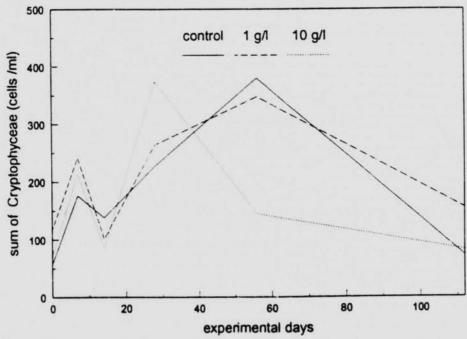


Figure 27: Fluctuations of density of Corptophyceae in the test ponds

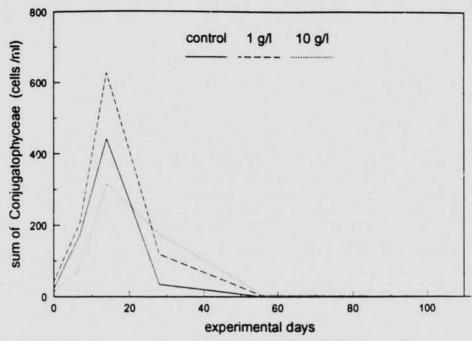


Figure 28: Fluctuations of density of Conjugatophyceae in the test ponds

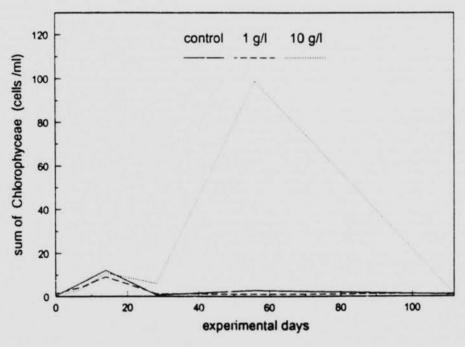


Figure 29: Flurtuations of density of Chlorophyceae in the test ponds

3.4.3 Comparison of Phytoplankton Communities

3.4.3.1 Total Number of Phytoplankton Species and Shannon-Weaver-Diversity

Throughout the study period, a total of 53 phytoplankton species were identified in the artificial ponds (although not all individuals were identified to the species level), comprising six major taxonomic groups: Cyanophyceae (at least 2 species), Diatomeae (20 species), Euglenophyceae (5 species), Cryptophyceae (4 species), Chlorophyceae (15 species) and Conjugatophyceae (7 species).

The total number of species in each pond were:

control at least 48 species 1 g/l (low dose) at least 47 species 10 g/l (high dose) at least 43 species

Of these species, however, the majority occurred only in low numbers on a few sampling dates. The population dynamics of the three main groups - Cryptophyceae, Chlorophyceae and Conjugatophyceae - are presented in Figures 27 to 29. All raw data of phytoplankton organisms are listed in appendix III.

Figures 30 - 32 indicate the species composition of the test ponds. While the compostion of the control and low dosed pond was similar for the whole study period, the high dosed pond showed increasing differences after about 1 month following application. This can also be seen by the similarity index (as discussed in 3.4.3.2).

Although the number of species corresponded in the three ponds up to day 14, slight differences were observed in the fluctuations of taxonomic richness throughout the remaining study (Figure 33). After a minimum on day 56, the number of species increased in the control, while remaining at this level in the low dosed pond until day 112. In the high dosed pond the taxonomic richness decreased continuously from a maximum on day 28 to the end of the study. These differences cannot be interpreted as a test substance effect, as they represent natural fluctuations between the test ponds.

Observed fluctuations of Shannon-Weaver diversity index and eveness (Figures 34 and 35) in the test ponds are generally consistent between control and dosed ponds during the study, with the exception of the last sampling date (day 112). The high dosed pond distincly shows higher diversity at these sampling dates than the other ponds, although no dose-effect relationship is given. Earlier studies performed in these ponds with no application of a chemical demonstrated similar biocoenosis development for 8 - 10 weeks following separation and distinct differences the eafter (HEIMBACH et al. 1992; HEIMBACH 1993; HEIMBACH et al. 1993). The findings in this study, therefore, should not be over-interpreted. On the other hand, the different physico-chemical properties of the water in the study which is reported here caused different composition of organisms in the ponds but did obviously not affect the species diversity.

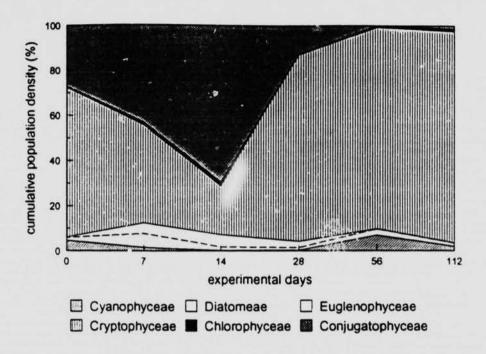


Figure 30: Cumulative phytoplankton density in the control pond

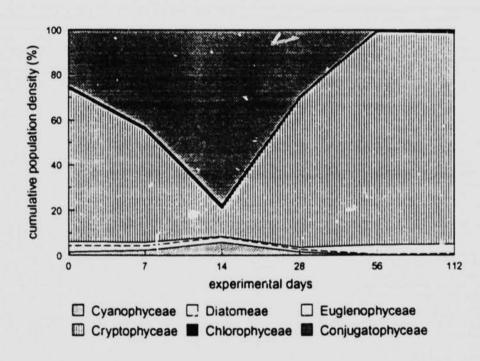


Figure 31: Cumulative phytoplankton density in the low dosed pond

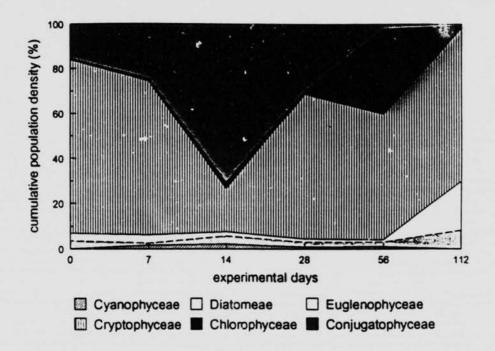


Figure 32: Cumulative phytoplankton density in the high dosed pond

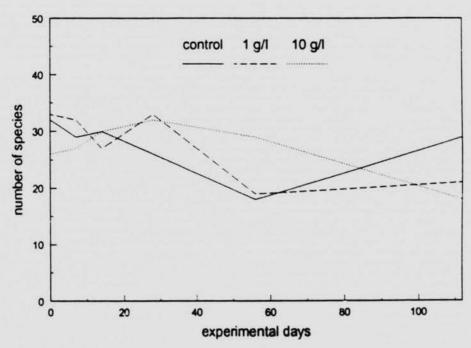


Figure 33: Changes in total number of phytoplankton species in the test ponds

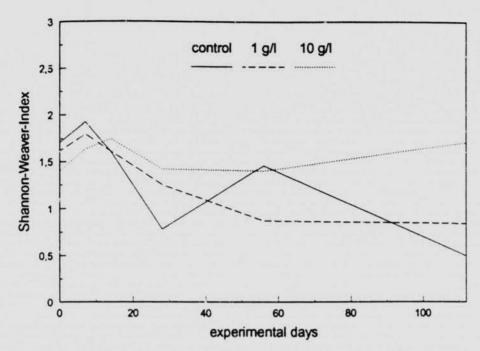


Figure 34: Fluctuations of the Shannon-Weaver-Index of diversity related to phytoplankton communities in the test ponds

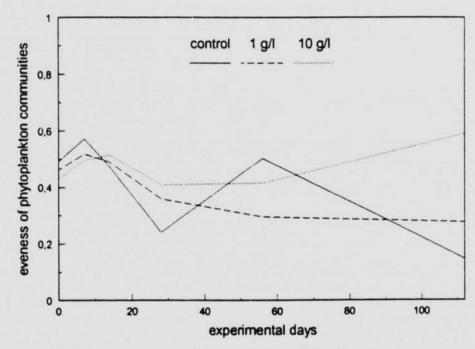


Figure 35: Fluctuations of the Eveness-Index of diversity related to phytoplankton communities in the test ponds

The Stander's Index, combined with a statistical procedure proposed by SMITH & MERCANTE (1989), yields an L-value which is a statistical value quantifying the similarity between two ponds. Due to the method of calculation, the index allows a comparison of community structure between ponds which is considerably more differentiated and statistically sound (see also 2.8) than the Shannon-Weaver-Index of diversity for example L-values equal to 1 indicate total similarity and are calculated when communities in two ponds are "identical".

Calculated similarity values of phytoplankton communities in control and the respective data of the dosed ponds (Figure 36 and 37) indicate very similar ("identical") community structures during application and the next 4 weeks. Thereafter, similarity slowly declines to L-values of about 0.8 on day 56 below the statistical critical limits of 5 and 1 %. At the termination of the study, similarity between control and dosed ponds increases to L-values of 1.0 in the low dosed pond but stays constant in the high dosed pond. The figures prove that no short-term effect from the treatment ensued, but some long-term effects cannot be excluded. These longterm effects, which were only pronounced in the high dosed pond, were most likely caused by different species compostion in the ponds 1 to 3 months after treatment. Additionally, the similarity between trea and ponds (Figure 38) confirms a long-term effect in the high dose from MDI on the species composition of phytoplankton organisms. The comparable development of algae structure in the dosed ponds during the first 2 months reveals that differences of similarity between the high dosed pond and the other ponds at the end of the study might be a secondary effect related to MDI treatment. Nevertheless, it must be noted that earlier studies in these ponds demonstrated differences following an 8 - 10 week period after the ponds were separated despite lack of application of a test substance (HEIMBACH et al. 1992; HEIMBACH 1993, HEIMBACH et al. 1993). As the species composition data (Figures 30 -32) also reflects the similarity index findings, a treatment related effect from the high dose of MDI on the phytoplankton community 1 to 4 months after application can be implied.

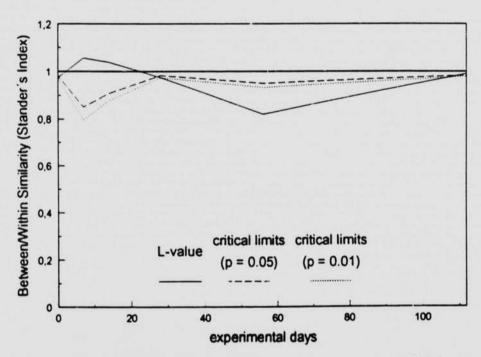


Figure 36: Similarity (Stander's Index) of phytoplankton communities between control and low dosed pond

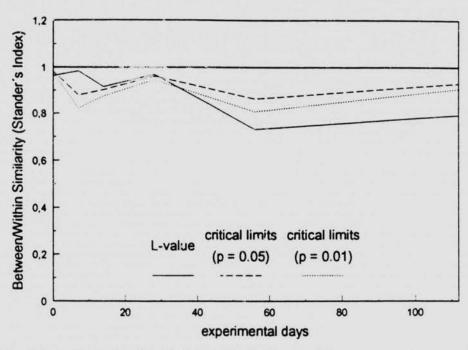


Figure 37: Similarity (Stander's Index) of phytoplankton communities between control and high dosed pond

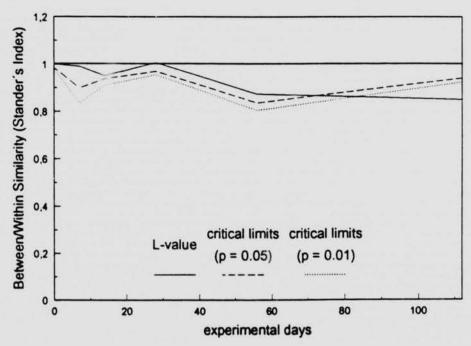


Figure 38: Similarity (Stander's Index) of phytoplankton communities between low and high dosed pond

3.4.4 Zooplankton

The sum of zooplankton species (Figure 39) shows about 100 to 200 organisms per litre throughout the study period, with an increase in numbers in the high dosed pond at the end of the study to about 900 individuals /1.

A variety of 19 zooplankton species were identified in the ponds, although not all individuals were identified to a species level. The zooplankton in the test ponds comprised at least 8 species of the order Cladocera (although juvenile organisms were not identified to species level), 3 species of Copepoda (although juvenile organisms were not identified to species level), and at least 8 species of Rotatoria; Ostracoda could not be identified to species level as only juveniles were detected.

The total number of zooplankton species in different test ponds were:

control	at least	15	species
1 g/l	at least	18	species
10 g/l	at least	17	species

Some insect larvae (Chironomidae and Chaoborus sp.) were also found in the zooplankton samples. Because only a few individuals were detected, these findings are considered accidental and are consequently not included in the following discussion. The population dynamics of the three main groups - Cladocera, Copepoda and Rotatoria - are presented in Figures 40, 41 and 42, respectively. All raw data of zooplankton organisms are listed in appendix III.

Cladocera consisted mainly of juvenile stages, while some individuals of Daphnia longispina, Simocephalus vetulus, Chydorus sphaericus and Daphnia magna were identified. The total number of Cladocera increased in all ponds to a maximum 1 to 2 weeks after application (juvenile daphnids mainly) and decreased thereafter to about 20 to 40 individuals/l in all ponds for the rest of the study (Figure 40). The Cladocera abundance was slightly reduced in the high dosed pond 2 - 8 weeks after application as compared to the control pond. No further differences between treatments can be recognised, although the low dosed pond shows the same tendency.

Copepodite and their juvenile naupliae were the dominant Copepoda. During the most part of the study the density was consistent between both dosed ponds with some fluctuations and a peak in the high dosed pond on day 112 (Figure 41). At the termination of the study, copepod density in the treated ponds increased slightly with maximum numbers of naupliae in the high dosed pond. Control density mostly decreased in comparison to the treated ponds.

Polyarthra remata, Keratella quadrata and Synchaeta sp. were the dominant rotifer species in the three ponds. Generally rotifer population densities were consistent between control and dosed ponds, with peaks on days 14 and 112 in the high dosed pond (Figure 42). These peaks were caused by the overwhelming abundance of Keratella quadrata and Polyarthra remata.

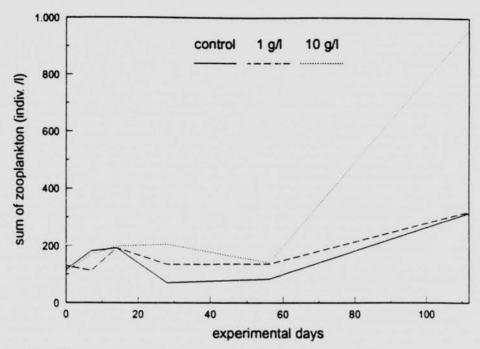


Figure 39: Fluctuations of zooplankton density in the test ponds

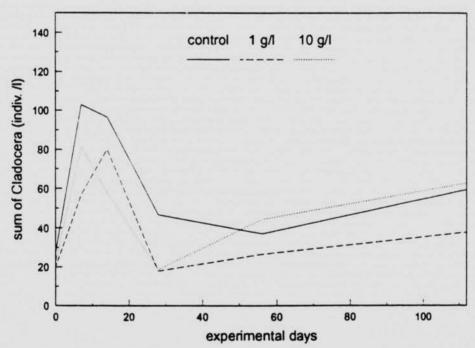


Figure 40: Fluctuations of population density of Cladocera in the test ponds

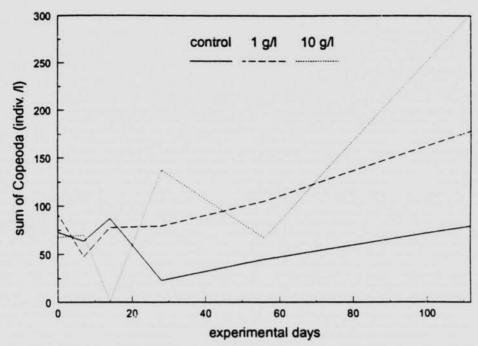


Figure 41: Fluctuations of population density of Copepoda in the test ponds

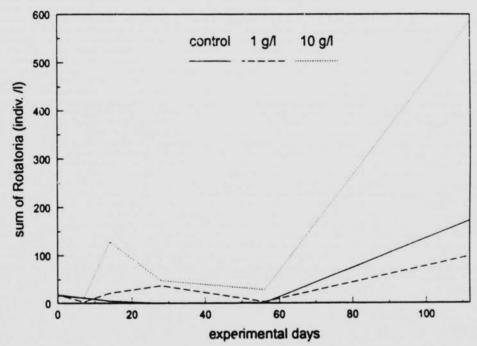


Figure 42: Fluctuations of population density of Rotatoria in the test ponds

3.4.5 Comparison of Zooplankton Communities

3.4.5.1 Total Number of Zooplankton Species and Shannon-Weaver-Diversity

Zooplankton taxonomic richness ranged between 7 and 13 species identified on the different sampling dates (Figure 43). Taxonomic richness of the treated ponds was very similar during the study, it increased from 9 identified species on day 0 to 12 and 13 species, on day 28 and remained at about this level until the end of the study. The number of species in the control decreased to 7 on day 28, and remained at about this level until day 112, when 9 species were identified. No apparent differences were observed between the ponds during the study. Highest observed taxonomic richness occurred in the low dosed pond on day 28.

Species composition (Figures 44 - 46) shows similar trends in the control pond and the low dosed pond. Contrary, the high dosed pond shows greater abundance of Rotatoria throughout the study, especially on days 14 and 56 -112 (see also Figure 42).

The Shannon-Weaver-Diversity Index (Figure 47) and the eveness (Figure 48) of the zooplankton communities are quite similar in all ponds at the start of the study. After a slight increase in the first two weeks following application in all ponds, the indices fluctuate slightly without any recognizable trend within or between treatments for the rest of the study. Overall, there is no indication of adverse effects from the treatment c zooplankton diversity.

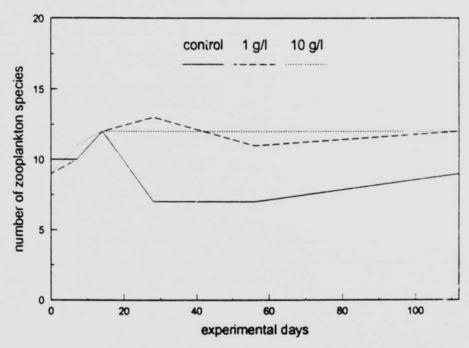


Figure 43: Fluctuations in the total number of zooplankton species in the test ponds

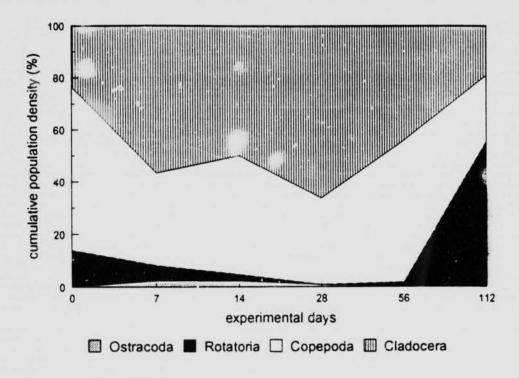


Figure 44: Cumulative zooplankton density in the control pond

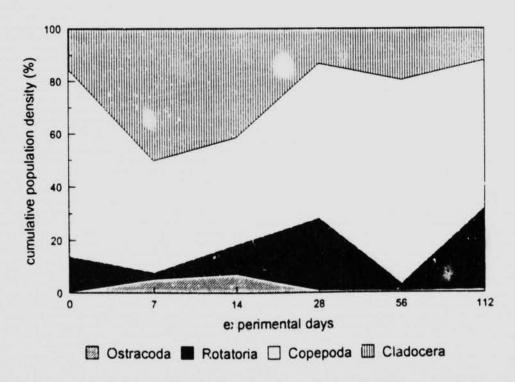


Figure 45: Cumulative zooplankton density in the low dosed pond

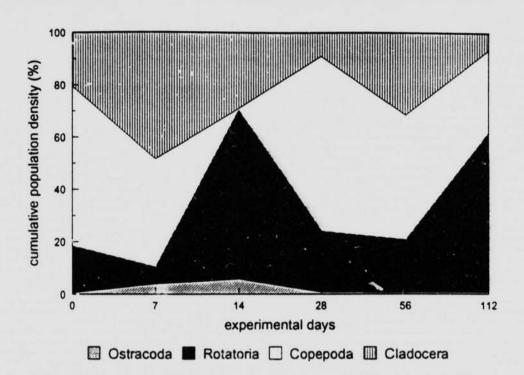


Figure 46: Cumulative zooplankton density in the high dosed pond

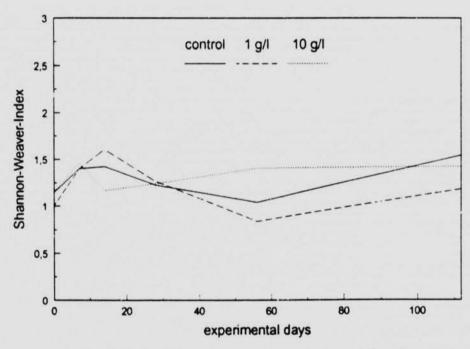


Figure 47: Fluctuations of the Shannon-Weaver-Index of diversity calculated for the zooplankton communities in the test ponds

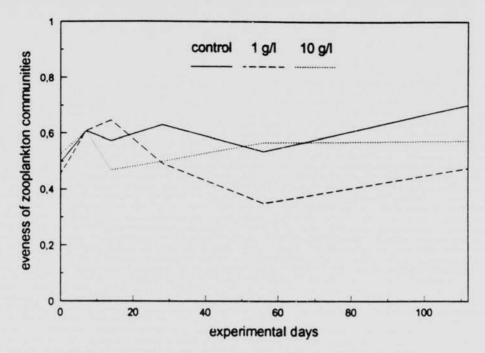


Figure 48: Eveness of zooplankton communities in the test ponds

3.4.5.2 Similarity of Zooplankton Communities (Stander's Index)

F llowing application, zooplankton similarity between control and low dosed pond (Figure 49) ucclines slightly from about 1.0 to about 0.6 on day 28, which is well below the statistical significance levels of P=1 and 5%. Thereafter, similarity increases to 0.9 on day 56 (equivalent to the statistical level of P=1%) and about 0.8 on day 112. Comparison of control and high dosed pond communities shows similar results (Figure 50). The calculated values indicate close similarity between communities of control and high dosed ponds during the first 1 to 2 weeks of the study. The similarity decreases thereafter to statistically significantly lower values of approximately 0.2, but reaches maximum numbers again of approximately 0.6 after about 1 month and approximately 0.9 after about 2 months (equivalent to the statistical level of P=5%) for the remaining study. In summary, both ponds show a decrease in similarity in comparison to the control pond after the first weeks of the study only (Figure 51). The differences from the control pond are greater in the high dosed pond than in the low dosed one. After about 2 months, the similarity between all ponds is considered statistically significantly great, indicating no further direct or indirect long-term effects from application of MDI.

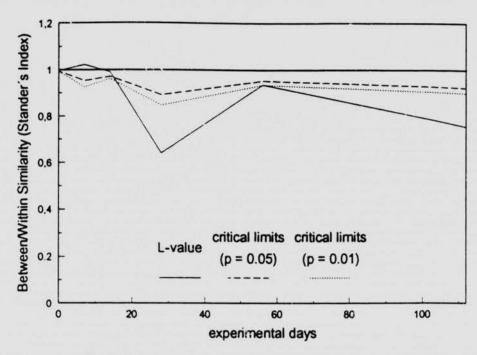


Figure 49: Similarity (Stander's Index) of zooplankton communities in control and low dosed pond

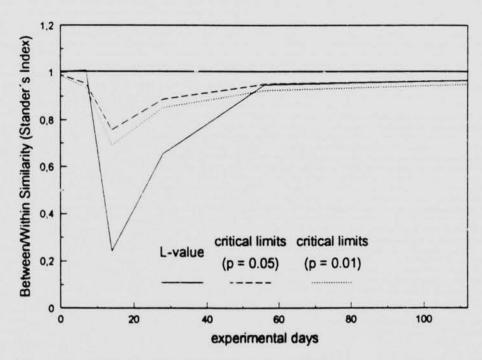


Figure 50: Similarity (Stander's Index) of zooplankton mmunities in control and high dosed pond

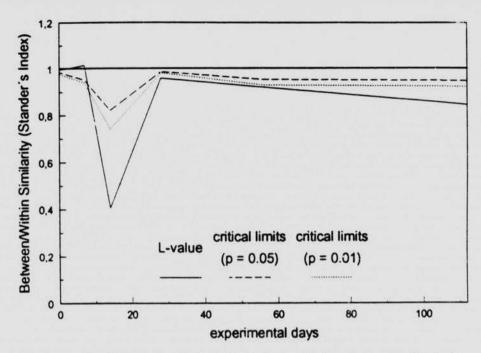


Figure 51: Similarity (Stander's Index) of zooplankton communities in low and high dosed pond

3.4.6 Macrobenthos

The sum of macrobenthos individuals (Figure 52) is about 10,000 to 30,000 organisms per m², with a slight increase in numbers in all ponds throughout the study. As these results are mainly caused by the overwhelming abundance of Tubificidae (Figure 53), they cannot be solely discussed.

A variety of 7 macrobenthos species (Oligochaeta, Hirudinaea, Gastropoda, Bivalvia, Ephemeroptera and Diptera) were identified in the ponds, although not all individuals were identified to the species level. The macrobenthos in the test ponds comprised 2 species of Hirudinaea (Erpobdella octoculata, Helobdella stagnalis), 2 species of Gastropoda (Radix peregra, Gyraulus albus), 2 species of Bivalvia (Sphaerium sp., Pisidium sp.), and 1 species of Ephemeroptera (Cloeon dipterum). All other organisms (Tubificidae, Naididae, Ostracoda, Chaoberidae and Chironomidae) could not be identified to a species level.

The total number of benthic species in different test ponds were (some of these species have not been identified to a species level):

control	at least	11	species
1 g/l	at least	13	species
10 g/l	at least	11	species

Some insect larvae (Chironomidae and Chaoborus sp.) were also found in the zooplankton samples. Because only a few individuals could be detected in the zooplankton samples, these findings are considered accidental and therefore not included in the zooplankton discussion. The population dynamics of the 4 main groups of macrobenthos - Tubificidae, Naididae, Bivalvia and Diptera - are presented in Figures 53 - 56. Fair raw data of benthic organisms are listed in appendix III. Ostracoda findings are considered accidental in macrobenthos samples and are therefore not included in macrobenthos discussions.

The majority of macrobenthos organisms were the Oligochaeta Tubificidae (Figure 53) and Naididae (Figure 54), representing about 90 % of benthic organisms in all ponds (Figure 58 -60). The total number of Oligochaeta in the control and low dosed ponds fluctuated around 20,000 organisms / m². Contrary, the numbers of these organisms decreased in the high dosed pond until day 7 to a low number of 280 individuals / m² and increased slightly throughout the remaining study to numbers which were similar to the two other ponds. This decrease is attributed to the fact that a great portion of the test compound reached the untreated half of the pond sediment (see 2.5.3.7 and 3.5.1), so that on average approximately 50 % of the samples consisted of test substance. The data presented in Figures 52 - 56 have not been changed accordingly. Nevertheless, the results indicate test substance related effects on the population abundance of these organisms. As the test substance polymerized during the first weeks of the study, forming CO2-bubbles which floated to the water surface, some test substance was constantly being lifted from sediment surface, broken up and transported to other areas of the sediment (3.5.1). In consequence, the test substance was continuously being transported to other parts of the sediment. This physical effect killed many sediment-dwelling organisms during the first weeks of the study. The postulated elevated CO₂-concentration at the sediment/water interface may also have intensified this effect. The abundance of Oligochaeta increased after the first 1 - 2 weeks following application, demonstrating that these populations recovered very well, despite the presence of test substance in their habitat. As the polymerization process was completed after some weeks following application, a stable layer of hardened test substance covered part of the sediment. At this point the surviving organisms built up population densities equal to that in the control pond.

The abundance of Bivalvia (Figure 55) (Sphaerium sp. and Pisidium sp.) was similar only for the first 2 weeks of the study in the control and low dosed pond. The low dosed pond showed a slight decrease from day 7 to day 14 with an immediate increase the lafter. As the control pond showed similar fluctuations throughout the study, a treatment related effect cannot be interpreted. However, there was a steady decline in organism numbers in the low dosed pond from day 28 to the end of the study. The data cannot be interpreted with regard to effects on these organisms as the natural fluctuation is far too high. In contrary, the high dosed pond showed a distinct decline in Bivalvia numbers during the first weeks after application and no recovery of the population thereafter. The decline was a direct physical effect. It may have been also indirectly caused by high CO2-concentrations as discussed above for the Oligochaeta. However, because Bivalvia do not reproduce as quickly as Oligochaeta or Diptera (see below), the populations could not recover within the remaining weeks of the study.

The Diptera (mainly Chironomidae and Tanypodinae, me Chaoberidae and Orthocladiinae) show no population effects on density in the low dosed pond (Figure 56). For the same reasons given above, the population densities of Diptera decreased drastically in the high dosed pond during the first week after application. Contrary to the Bivalvia, populations recovered after about 3 - 4 weeks and achieved numbers similar to the control and low dosed ponds after about 3 months. The generation time of these organisms is short, therefore accounting for the rebound in population density.

Gastropoda could be identified very rarely in the sediment samples. Gastropoda are mobile organisms. They are able to move to those parts of the sediment or pond walls which are not covered by the test substance. As they were found in all ponds at all parts of the study, treatment related effects are excluded.

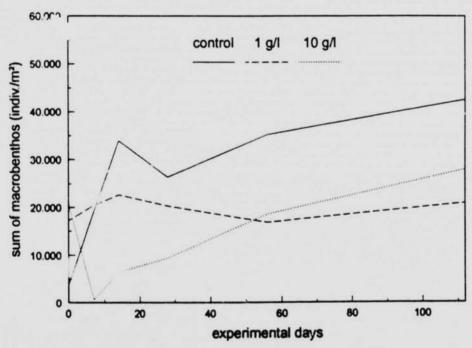


Figure 52: Fluctuations of macrobenthos density in the test ponds

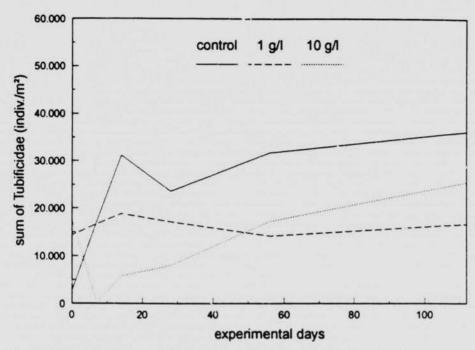


Figure 53: Fluctuations of population density of Tubificidae in the test ponds

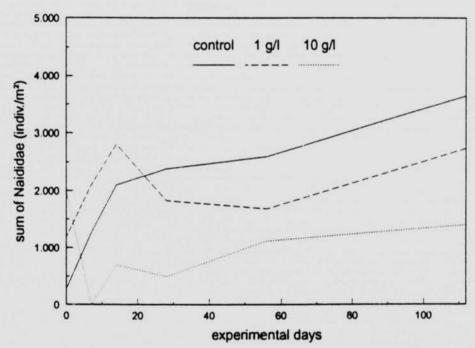


Figure 54: Fluctuations of population density of Naididae in the test ponds

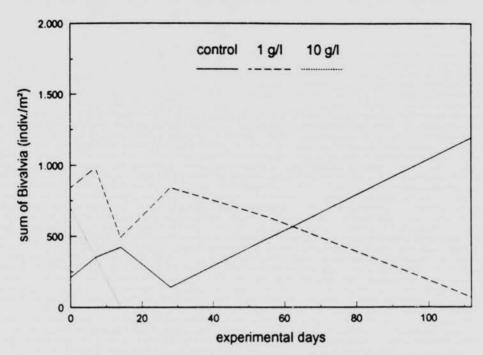


Figure 55: Fluctuations of population density of Bivalvia in the test ponds

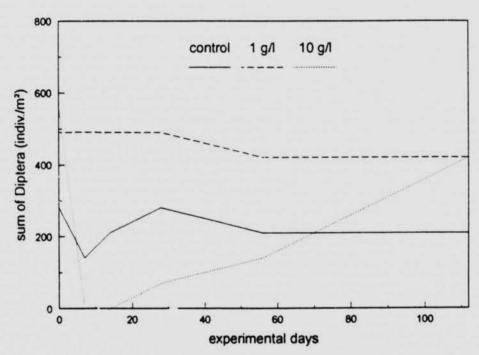


Figure 56: Fluctuations of population density of Diptera in the test ponds

3.4.7 Comparison of Macrobenthos Communities

3.4.7.1 Total Number of Macrobenthos Species and Shannon-Weaver-Diversity

Macrobenthos taxonomic richness ranged between 2 and 11 species on the different sampling dates (Figure 57). After a slight decrease in taxonomic richness in the control pond in the first month following application, the number of identified species increased slightly thereafter. While the low dosed pond showed a similar trend, the number of species in the high dosed pond were clearly lower 2 - 3 weeks after application, but increased steadily thereafter to similar numbers as in the other ponds. Except for this short-term reduction in the beginning of the study (as discussed in 3.4.6), no apparent differences were observed between the ponds during the study. Highest observed taxonomic richness occurred in the low dosed pond on day 112.

Species composition (Figures 58 - 60) shows similar trends in the control pond and the low dosed pond. Contrary, the high dosed pond shows a relatively high abundancy of Bivalvia 7 days after application, although Bivalvia abundances were markedly reduced after 14 days.

The Shannon-Weaver-Diversity Index (Figure 61) and the eveness of the macrobenthos communities (Figure 62) are quite similar in all ponds at the start of the study. After some fluctuations in the first weeks following application in all ponds, the indices remain quite constant with no recognizable trends within or between treatments for the remaining study. Overall, there is no indication of adverse effects from treatment on macrobenthos diversity.

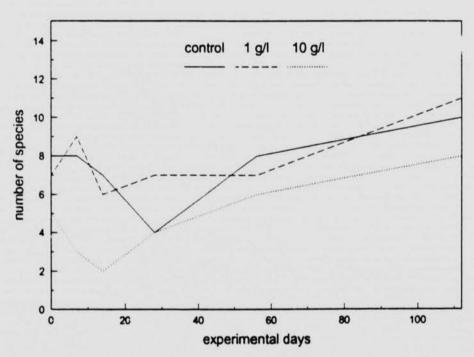


Figure 57: Fluctuations in the total number of macrobenthos species in the test ponds

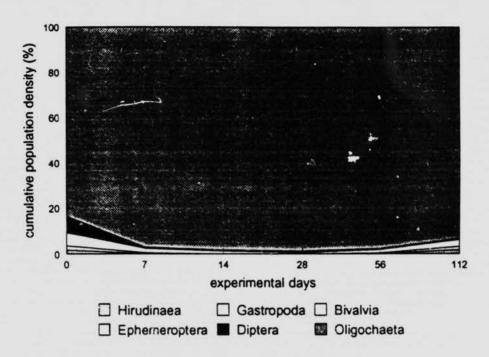


Figure 58: Cumulative macrobenthos density in the control pond

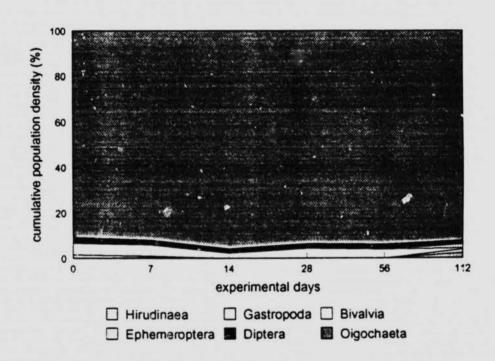


Figure 59: Cumulative macrobenthos density in the low dosed pond

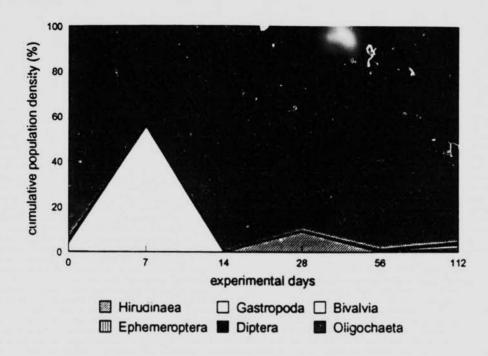


Figure 60: Cumulative macrobenthos density in the high dosed pond

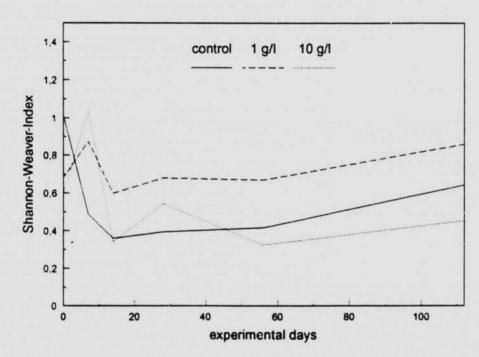


Figure 61: Fluctuations of the Shannon-Weaver-Index of diversity calculated for the macrobenthos communities in the test ponds

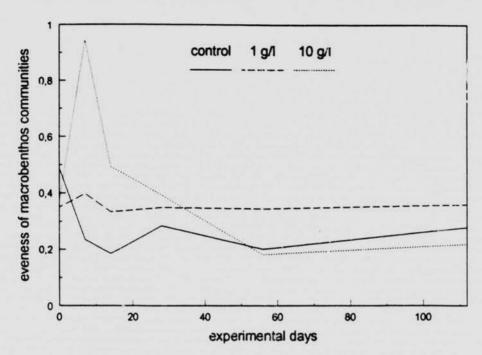


Figure 62: Eveness of macrobenthos communities in the test ponds

3.4.7.2 Similarity of Macrobenthos Communities (Stander's Index)

Following application, benthic similarity between control and low dosed ponds (Figure 63) do not show any treatment related effects for the whole study period (L-values well above 5 and 1 % critical values). Comparison of control and high dosed pond communities, however, show a different picture (Figure 64). The calculated values decrease 7 and 28 days after application well below the critical limits, indicating biological differences between the benthic biocoenosis of these ponds. These findings represent the results of species composition as discussed earlier. The high dosed pond shows a decrease in similarity in comparison to the control pond for the first weeks of the study only. After about 2 months, the similarity between these ponds increases to L-values of approximately 1.0 indicating no further long-term effects from application of MDI. The similarity between the low and the high dosed ponds (Figure 65) confirms the statements on effects in the high dosed pond.

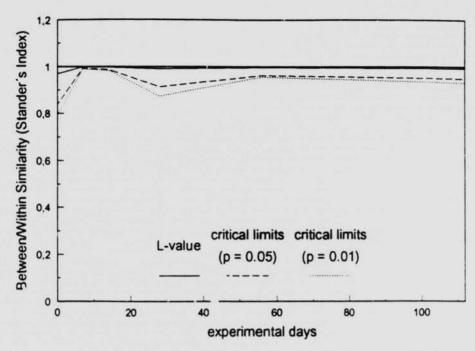


Figure 63: Similarity (Stander's Index) of macrobenthos communities in control and low dosed pond

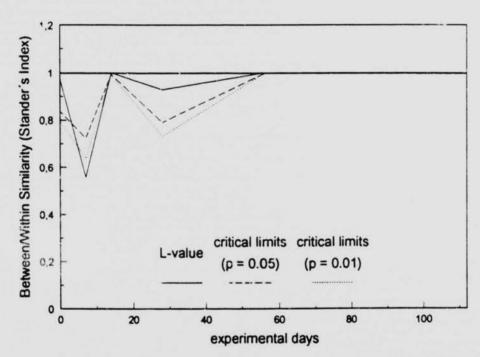


Figure 64: Similarity (Stander's Index) of macrobenthos communities in control and high dosed pend

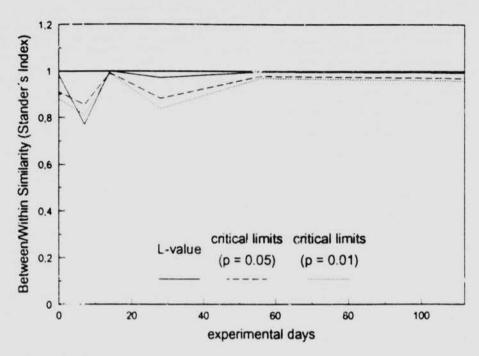


Figure 65: Similarity (Stander's Index) of macrobenthos communities in low and high dosed pond

3.4.8 Fish

To allow adaptation to the test conditions, each pond was stocked with 6 trout 56 days before the treatment. The average body weight of the trout in each pond ranged between 6.6 to 6.8 g and the average body length was 8.2 cm.

The condition factor of the test fish was calculated with the formular:

condition factor = weight * 100 / length³.

During the study, 3 fish died in the high dosed pond (between days 30 - 35). They were replaced by new fish of the same stock held under laboratory conditions (see 2.5.1.2) on day 40. This mortality was caused by the limited food supply during the first weeks of the study. As the trout were kept in cages and a filumentous film of green algae grew on top of the cages, the trout relied on a decreasing number of zooplankton organisms which could not move into the cages very easily. In consequence, the trout did not get enough food and lost weight (Figure 67). This effect was enhanced by the very low numbers of Cladocera in the high dosed pond 2 weeks after application which are the main food supply for the fish. In addition, the filamentous green algae on the cages in the high dosed pond built a more intensive film as in the other ponds, similar to macrophyte growth (3.4.9). Although fish were fed some artificial commercial fish food as soon as the problem was recognized on day 28, some fish in the high dosed pond did not recover and died a few days later. The reduced pH is not considered the cause of fish mortality, as the pH was well above pH 5 which is considered to be the toxic threshold for rainbow trout. In addition, all other fish recovered immediately after the addition of artificial fish food and showed a constant weight and length increase for the rest of the study, although pH remained quite low in the high dosed pond for about 4 more weeks (pH 6.1 - 6.4 above the sediment).

In the low dosed pond, one fish was injured by mechanical handling on day 69 (determination of body length and weight). The fish did not recover and was found with symptoms on day 91 and dead on day 93. (It must be mentioned that fish condition could not be observed visually every lay in order to avoid high mortality even in the control pond.) All other fish in the 3 ponds did not show any symptoms or abnormal behaviour throughout the study.

Figures 66 - 68 and Tables 7 - 9 show the average values of body length and weight and the condition factor of the test fish. For these calculations, those trout which replaced dead ones were not used. Therefore, the data are based on: n = 6 trout in the high dosed pond until day 28 when 3 trout are used; n = 6 trout in the low dosed pond until day 69 when 5 trout are used (although the sixth fish was still alive on day 91 it was not considered for the mean values of this day, as the fish already showed notable symptoms); and, n = 6 trout for the whole study in the control.

Due to the exposure in cages, the supply of natural food was considerably restricted. Therefore, the weight and condition factor of all fish decreased continuously until day 28 (rigure 68). While the body length of fish in the low dosed pond and control pond were very similar for the whole study, the fish of the high dosed pond were distinctly lighter than those of the control after day 20, caused by an even more reduced food supply in the high dosed pond (as discussed above). After addition of artificial fish food, the body weight of all fish increased steadily in all ponds, confirming the conclusion that the observed effects on fish in the high dosed pond were caused secondarily and cannot be interpreted as a toxic effect from the test substance. Free swimming fish would not have shown these differences between treatments, as the fish would have been able to swim around to get enough food.

<u>Table 7</u> Average body length of fish (cm)
(The corresponding numbers of fish are given in 3.4.8.)

Experimen- tal Dav	Date	Control Pond		Pond 1g/l		Pond 10 g/l	
		mean	standard deviation	mean	standard deviation	mean	standard deviation
-56	March 18, 1992	8.15	0.30	8.17	0.45	8.22	0.32
- 1	May 12	8.82	0.45	8.67	0.45	8.95	0.53
7	May 20	8.78	0.48	8.73	0.41	8.97	0.52
14	May 27	8.82	0.48	8.73	0.41	8.85	0.50
28	June 10	8.65	0.33	8.45	0.41	8.62	0.38
48	June 30	8.98	0.50	8.52	0.41	8.80	0.66
56	July 8	9.00	0.43	8.83	0.36	9.23	0.74
69	July 21	9.15	0.48	9.00	0.47	9.17	0.45
91	August 12	9.27	0.53	9.10	0.58	9.27	0.31
112	September 2	9.42	0.47	9.40	0.82	9.20	0.42

Table 8: Average body weight of fish (g)
(The corresponding numbers of fish are given in 3.4.8.)

24.

Experimen- tal Day	Date	Control Pond		Pond 1g/l		Pond 10 g/l	
		mean	standard deviation	mean	standard deviation	mean	standard deviation
-56	March 18, 1992	6.57	1.28	6.67	1.21	6.75	0.97
- 1	May 12	6.22	1.13	6.08	0.84	6.55	1.01
7	May 20	6.00	1.11	5.80	0.98	6.28	1.37
14	May 27	5.65	1.08	5.37	0.65	5.55	0.97
28	June 10	5.73	1.14	5.20	0.57	4.80	1.02
48	June 30	7.20	1.52	5.73	0.66	5.30	0.95
56	July 8	7.45	1.43	6.52	0.86	5.80	0.89
69	July 21	7.62	1.50	7.32	1.07	6.87	1.46
91	August 12	8.48	1.55	8.18	1.55	7.63	0.72
112	September 2	8.47	1.19	8.54	1.65	7.13	0.64

Table 9: Average condition factor of fish (condition factor = weight * 100 / length³)
(The corresponding numbers of fish are given in 3.4.8.)

Experimen- tal Day	Date	Control Pond		Pond 1g/l		Pond 10 g/l	
		mean	standard deviation	mean	standard deviation	mean	standard deviation
-56	March 18, 1992	1.21	0.17	1.21	0.09	1.21	0.06
1	May 12	0.90	0.06	0.93	0.03	0.91	0.10
7	May 20	0.88	0.07	0.86	0.06	0.86	0.06
14	May 27	0.82	0.09	0.80	0.03	0.80	0.07
28	June 10	0.88	0.09	0.86	0.07	0.74	0.08
48	June 30	0.98	0.08	0.93	0.07	0.77	0.05
56	July 8	1.01	0.07	0.94	0.09	0.74	0.08
69	July 21	0.98	0.05	1.00	0.09	0.88	0.12
91	August 12	1.06	0.06	1.08	0.04	0.96	0.06
112	September 2	1.01	0.05	1.03	0.11	0.92	0.05

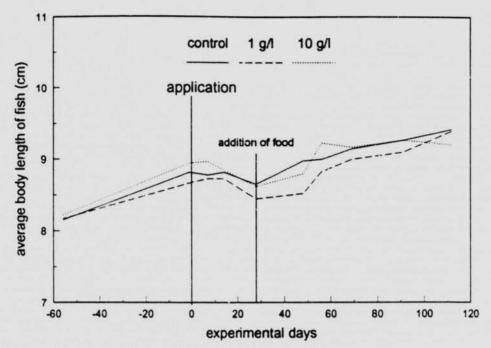


Figure 66: Average length of trout in the test ponds

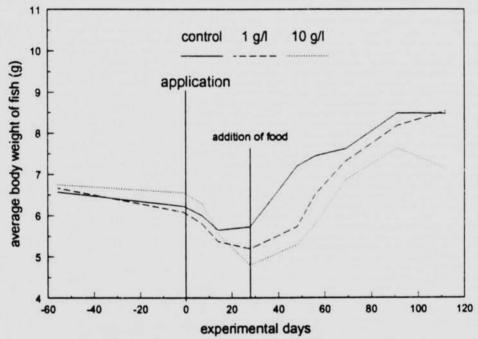


Figure 67: Average weight of trout in the test ponds

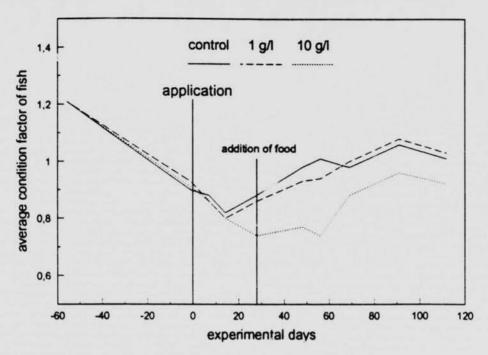


Figure 68: Average condition factor of trout in the test ponds

3.4.9 Aquatic Macrophytes

The natural sediment applied to the artificial ponds contained seeds, spores and winter buds of aquatic macrophytes. During the vegetation period only two species of submerged aquatic macrophytes were recorded, Zannichellia palustris and Potamogeton crispus, and these were the dominant aquatic macrophyte in the study. Due to missing banks, no emerging macrophytes colonized the ponds.

From time to time the macrophytes were removed from the ponds and their biomass was determined (see 2.5.3.7). As it was not possible to remove all macrophytes from a pond due to water turbidity, the biomass data (Table 10) cannot be considered quantitative in terms of macrophyte abundancy at each sampling event. Nevertheless, as the macrophytes were removed comparably carefully at each sampling date in all ponds, the determined biomasses of macrophytes allows a comparison of macrophytes abundance within and between ponds.

The data in Table 10 prove that during the pretreatment period no differences between the ponds existed. During the first days following application no or very few macrophytes were observed in the high dosed pond, as they were depressed by the addition of the test substance on the sediment (3.5.1). Thereafter, a dose related intensified growth of macrophytes was recorded in the treated ponds. In the high dosed pond up to 40 times more biomass was determined on day 44 in comparison to control pond. In addition, leaves and stalks of the macrophytes in the high dosed pond were thicker compared to the control. The reason for the considerable growth of macrophytes in the high dosed pond is the increased supply of carbon dioxide (see 3.2.3 and 3.5.1), enabling a high primary production.

Table 10: Biomass of harvested macrophytes

		Biomass	(dry weight in g)	
Experimental Day	Date (1992)	Control	Pond 1 g/l	Pond 10 g/l
- 27	April 16	3.0	3.4	4.1
- 8	May 5	7.5	4.2	3.7
9	May 22	2.3	3.3	0 *)
16	May 29	0.8	6.0	11.4
20	June 2	1.2	4.0	10.1
33	June 15	2.5	1.2	15.0
44	June 26	1.0	3.2	39.0
76	July 28	13.2	19.7	60.0
118 **)	September 8	600	685	850
Sum	THE STREET	632	730	993

^{*)} not determined, as only one plant could be seen

**) The plants were removed after the ponds were emptied, some of them with roots

3.5 Residue Analysis

3.5.1 Fate of MDI in Test Ponds

The analytical results of this study depend substantially on the chemical characteristics and fate of MDI in water. As discribed in section 2.2, the applied polymeric MDI product is not stable in water, but reacts with water to form polyureas and carbon dioxide with only traces of MDA. In this study, the test compound was added to the sediment surface of the treated ponds. Due to the high specific gravity and viscosity of the test compound, it fell directly on top of the sediment in different areas of the pond, some parts were even covered by very soft sediment. As stated previously (2.5.2), approximately 30 % of the sediment of the treated section was covered in the low dosed pond (i.e. 15 % of the total sediment) at the end of the study. In the high dosed pond, about 90 % of the treated half was covered (some MDI, 40 % of the applied amount, even reached the part of the sediment which was intended to be kept untreated, see 2.5.2).

In the presence of water, the applied isocyanate polymerized at the interface between the product and water, producing carbon dioxide gr.s bubbles which floated to the water surface. In natural water ecosystems gas bubbles can always be observed; which are typically a combination of methane, oxygen and carbon dioxide which are not dissolved in water. In the high dosed pond in this study, however, notably more bubbles were recorded than occur in a natural ecosystem. Therefore, equipment was installed (a funnel attached to a bottle filled with pond water) to catch the bubbles in the high dosed and control ponds for 21 days (July 9 - 30, 1992, i.e. days 57 - 78). According to these findings, the bubbles in the high dosed pond contained 2 to 3 fold the CO₂ amount of the control pond. These data reveal a more proportional amount of non-dissolved carbon dioxide in the water of the high dosed pond than in the control pond.

As some carbon dioxide was also produced beneath the MDI layer, large gas bubbles gathered which were able to partly lift these layers. In consequence, the layers were fragmented into pieces of varying size. For the first 7 weeks of the study, this process continuously redistributed the test compound on the sediment surface. Smaller particles floated to the water surface, where some of them would sink down to the sediment again as a result of wheather conditions such as wind or rainfall. Other fragments formed larger particles due to the adhesive properties of the particle surface. With a few exceptions, the larger particles also sank down after several days. Nevertheless, some of them stuck to the walls of the ponds where they continuously polymerized.

3.5.2 Residues in Water

The applied substance was a commercial polymeric MDI product containing about 44 % 4,4'-MDI, with the balance being higher homologues and isomers. This product reacts with water to form polyureas, which are not soluble in water, and carbon dioxide with only traces of MDA (4,4'-diphenylmethane-diamine). Therefore, only MDA- and MDI-monomers were analyzed in water in this study.

3.5.3 Residues in Sediment

In each pond, a barrier made of stainless steel divided the sediment surface into two parts, each 1/2 of the total sediment surface. The barriers reached into the water for several centimeters, to prevent the test compound, which was added to one of these two parts, from flowing into the other part. Samples for analysis were only taken from the untreated part. In spite of the barrier in the high dosed pond, approximately 40 % of the applied amount flowed into the "untreated" part; this observation was further proven at the end of the study after the ponds were emptied. Both parts of the pond were covered with a 1 to 2 cm thick layer of the substance, in the treated part it was an uniform layer, in the untreated part it consisted of smaller fragmented pieces. Hence, a great amount of the substance was detected in the sediment of the "untreated" part (up to 21.5 g MDI/kg sediment, Table 14). On day 14, six individual samples were taken and analyzed in the high dosed pond, at all other sampling dates a mixture was taken and analyzed twice (sample I and II). The results of the individual samples on day 14 indicate a wide variation in content of MDI (from 0.5 to 21.5 g/kg). This variation is a reflection of the different thicknesses of the MDI-layer and its incongruous distribution in the untreated part of the pond. Therefore, a homogenous sampling of sediment was impossible. Nevertheless, the results indicate that MDI monomers were present in the sediment of this pond at relatively high concentrations. The concentrations steadily declined throughout the study (Table 14). Contrary, MDA was present only at very low concentrations in both treated ponds (Table 13).

In the low dosed pond fragments as large as 15×15 cm were found in the treated part at the end of the study after the pond was emptied. In the untreated part, however, no particles were observed. According to the analytical results, MDA was not detected in this pond at any sampling date except for one analysis on sample day 7 (Table 13). Some monomer MDI, however, was analyzed in these samples. The data indicate a wide variability between sampling dates (Table 14). The highest concentration was analyzed on day 7 (mean value of 7.6 mg/kg) with decreasing concentrations thereafter: 3.2 mg/kg on day 14, 1.4 mg/kg on day 28, 1.2 mg/kg on day 56 and \leq 0.7 mg/kg on day 112. The MDI originated in the low dosed pond from particles of the applied test substance which floated to the water surface and sank down onto the sediment of the untreated part, which is clearly demonstrated by the uneven distribution of MDI and MDA in the samples.

Detailed descriptions of the analytical methods and all individual analytical data are given in the analytical report in appendix V. In pretests, a mean rate of recovery of 82 % was determined for MDI and 56 % for MDA. The reported results are corrected for these rates of recovery. The limits of detection are 0.89 mg/kg (MDA) and 0.26 mg/kg (MDI-monomer).

Table 13: Results of residue analysis of MDA (4,4'-diphenylmethanediamine) in sediment

			MDA (mg	/kg)	
		Pond 1 g/		Pond 10	g/l
Experimen- tal Day	Date		mean values		mean values
-1	May 12, 1992	I: < 0.89 II: < 0.89	< 0.9	I: < 0.89 П: < 0.89	< 0.9
7	May 20	I: 22.9 II: < 0.89	≤ 11.9	I: 14.5 П: 60.5	37.5
14	May 27	I: < 0.89 II: < 0.89	< 0.9	I: < 0.89 П: < 0.89	< 0.9
28	June 10	I: < 0.89 II: < 0.89	< 0.9	I: 2.86 II: < 0.89	≤ 1.9
56	July 8	I: < 0.89 II: < 0.89	< 0.9	I: < 0.89 II: 3.75	≤ 2.3
112	September 2	I: < 0.89 II: < 0.89	< 0.9	I: < 0.89 II: < 0.89	< 0.9

Table 14: Results of residue analysis of the monomer MDI (4,4'-diphenylmethanediisocyanate) in sediment

			MDI (mg/	kg)	
		Pond 1 g/	1	Pond 10 g	Λ
Experimen- tal Day	Date	l line	mean values		mean values
-1	May 12, 1992	I: < 0.26 II: < 0.26	< 0.3	I: < 0.26 II: < 0.26	< 0.3
7	May 20	I: 13.5 II: 1.68	7.6	I: 10934 II: 9422	10200
14	May 27	I: 0.47 II: 5.87	3.2	1) 17793 2) 14960 3) 10426 4) 5262 5) 21535 6) 499	11700
28	June 10	I: 1.36 II: 1.42	1.4	I: 4122 II: 4132	4130
56	July 8	I: 1.68 II: 0.68	1.2	I: 1657 II: 2668	2160
112	September 2	I: < 0.26 II: 1.10	≤ 0.7	I: 0.68 П: 0.94	0.8

3.5.4 Residues in Fish

Neither MDA nor MDI were found in the analysis of fish at the end of the study. The limits of detection are 1.45 mg MDA /kg fish and 0.51 mg monomer MDI /kg fish respectively (Table 15).

<u>Table 15:</u> Results of residue analysis of MDA (4,4'-diphenylmethanediamine) and the monomer MDI (4,4'-diphenylmethanediisocyanate) in fish

		MDA		MDI	
Experimen- tal Day	Date	Pond 1 g/l (mg/kg)	Pond 10g/l (mg/kg)	Pond 1 g/l (mg/kg)	Pond 10 g/l (mg/kg)
0	May 13, 1992	n.a.	n.a.	n.a.	n.a.
112	September 2	< 1.45	< 1.45	< 0.51	< 0.51

n.a. = not analyzed

The numbers "< mg/l" indicate the limits of detection.

3.5.5 Review of Residue Situation

The monomer MDI on the potential reaction product MDA were not detected in water. The amounts of MDA and MDI analytically detected in pond water were below the detection limit. Both compounds did not accumulate in fish. The applied MDI polymerized and formed a stable non-uniform lumpy layer on the sediment surface of the ponds. At the end of the study, approximately 100 % of the applied substance was found in the sediment as hardened sheets of different sizes in the sediment.

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Referat GLP **Ouality Assurance Statement** Report No.: HBF/Mt 03 Study No.: E 413 0629-5 Title of report: Biological effects and fate of Desmodur 44 V 20 (polymeric MDI) in artificial ponds by simulating an accidental pollution The conduct of this study has been periodically inspected and this report has been audited by the Quality Assurance Unit. The dates of inspection are given below. Date of Protocol Inspection: Date of Report to Management: March 24, 1992 March 24, 1992 Date of Report to Management: Date of Study Inspection: May 13, 1992 May 14, 1992 June 10, 1992 June 11, 1992 September 2, 1992 September 9, 1992 September 9, 1992 October 6, 1992 October 7, 1992 Date of Final Report Audit: Date of Report to Management: June 22, 1993 July 1, 1993 The results reported in this study have been checked on the basis of our current SOPs and to the best of our knowledge accurately reflect the raw data.

(H. Schenk)

Quality Assurance Unit, PF-S

Date: fuly 1, 1993

Postanschrift: Postfach 300652, 4000 Düsseldorf Aktenzeichen: IV C 4 - 31.11.23.2

GLP-Bescheinigung

Bescheinigung	Certificate
Hiermit wird bestätigt, daß die Prüfungs- einrichtung	It is hereby certified that the test facility
Institut für Ökobiologie (OE)	Institut für Ökobiologie (OE)

Monheim in(Ort, Anschrift)	Nonheim in(location, address)
Bayer AG der(Firma)	Bayer AG of(company name)
19./20./22.02.1991	19./20./22.02.1991
em (Datum)	cn(âate)
von der für die Überwachung zuständigen Behörde über die Einhaltung der Grundsätze der Guten Laborpraxis inspiziert worden ist.	was inspected by the competent authority regarding compliance with the Principles of Good Laboratory Practice.
Es wird hiermit bestätigt, daß folgende Prüfungen in dieser Prüfeinrichtung nach den Grundsätzen der Guten Laborpraxis durchgeführt werden:	It is hereby certified that studies in this test facility are conducted in comliance with the Principles of Good Laboratory Practice.

Ökotoxikologische Untersuchungen zum Verbleib und zur Wirkung von Chemikalien (insbesondere Pflanzenschutzmitteln) an Pflanzen, Mikroorganismen, wirbellosen Tieren, χ) Wirbeltieren und Ökosystemen in Labor, Halbfreiland und Freiland.

Düsseldorf, den

20 .09.1951

In Vertretung

Dienstsiegel (official-seal)

(Dr. Baedeker)
- Staatssekretär -



English Translation

*) Ecotexicological investigations on the fate and effects of chemicals (especially pesticides) on plants, microorganisms, invertebrates, vertebrates and ecosystems in laboratory, semi-field and field studies.

Auswertung von

Phytoplankton, Zooplankton und Makrozoobenthos

im Rahmen von

Modeliteich-Versuchen

Studiennummer: E 413 0629-5

im Auftrag der

Bayer AG, Pflanzenschutzzentrum Monheim Abt. PF-F/UF-OE

durchgeführt von

aqua terra

Institut für angewandte Ökologie e.V. Wilhelmstraße 35a - 5000 Köln 50

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Für die Richtigkeit:

Lutta Hattman

Mahall Jandani

Köln, den 27.01.1993

Phy ankton - Modellteiche 13.05. - 02.01.1992 aqua ra 1992/ 203.1

1. Cvanophyceae:

COECU = Coelosohaerium kuetzingianum PSAAR = Pseudoanabaena articulata

2. Diatomeae:

ACNOR = Actinocyclus normanii AMPSP = Amphora spec. AULIT = Aulacoseira italica CALBA = Caloneis bacillum CYCME = Cyclotella menegheniana CYMVE = Cymbella ventricosa DIELO = Diatoma elongatum DIHIE = Diatoma hiemale DITEN = Diatoma tenuis DIVUL = Diatoma vulgaris FRACR = Fragilaria crotonensis GOMSP = Gomphonema spec. NACUS = Navicula cuspidata NAPER = Navicula peregrina NASUB = Navicula subrhynchocephala NASPC = Navicula spec. NICAP = Nitzschia capitellata NIFON = Nitzschia fonticola NILIN = Nitschia linearis NISUA = Nitzschia subacicularis PINME = Pinnularia mesolepta STANC = Stauroneis anceps SYNAC = Synedra acus DIUND = Diatomeen.undeterminiert

3. Euglenophyceae:

EUSPC = Euglena soec.
PHOSC = Phacus oscillans
PHPLE = Phacus pleuronectes
PHPYR = Phacus pyrum
TRSPC = Trachelomonas soec.

4. Cryptophyceae:

CRERO = Cryptomonas erosa/ovata
CRMAR = Cryptomonas Marssonii
CHNOR = Chroomonas nordstedti
RHOLA = Rhodomonas lacustris

5. Chlorophyceae:

COLMI = Coelastrum microporum COCFO = Coenococcus fottii DICPU = Dictyosphaerium pulchellum LAGGE = Lagerheimia genevansis KIRSU = Kirchneriella subcapitata OOSPC = Oocystis spec. PLALA = Planctonema lauterbornii SCARC = Scenedesmus arcuatus SCARM = Scenedesmus armatus SCART = Scenedesmus arthodesmi ormis

SANGER SANGER

SCELL = Scenedesmus ellipticus
SCOBL = Scenedesmus obliqus
SCSEM = Scenedesmus sempervirens
TECAU = Tetraed.on caudatum
TEKOM = Tetrastrum komarekii
CHLUN = Chlorophyceen, undeterminiert

6. Conjugatophyceae:

service with

CSEHR = Closterium ehrenbergii CSLUN = Closterium lunula

CSPRI = Closterium pritchardianum

CSPRO = Closterium pronum
COLAE = Cosmarium laeve
COMEN = Cosmarium meneghenii
PSSSP = Pseudostaurastrum soec.

CJUND = Conjugatophyceen. undeterminiert

CYANO = Summe der Cyanophyceae
DIATO = Summe der Diatomeze
EUGLE = Summe der Euglenophyceae
CRYPT = Summe der Cryptophyceae
CHLOR = Summe der Chlorophyceae
CONJU = Summe der Conjugatophyceae

ALGEN = Gesamtsumme der Algen

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T	P	DATUM	TAG	MICAP	MIFON	MISUA	STANC	SYNAC	ONUIO	EUSPC	PHOSC	PHPLE	PHPYR	TRSPC	CRERO	CRMAR	CHNOR	AJCHR
	1	130592	0	0.0	0.2	0.4	0.0	0.0	0.2	0.0	2.8	3.4	0.0	0.0	1.5	14.6	21.1	0.0
A	2	130592	0	0.2	0.1	0.4	0.0	0.0	0.1	0.0	3.5	0.6	0.0	0.0	0.0	17.3	28.8	0.0
٨	3	130592	0	0.0	0.3	0.4	0.0	0.0	0.2	0.1	1.2	0.9	0.0	6.0	3.1	16.5	34.7	0.0
	4	130592	0	0.0	0.0	9.1	0.0	0.0	0.0	0.0	4.7	2.0	0.0	0.0	0.0	19.4	35.9	0.0
	5	130592	0	0.0	0.4	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	4.3	19.5	40.1	0.0
1	6	130592	0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	4.1	1.1	0.0	0.0	1.5	16.9	62.4	0.0
A	1	200592	1	0.0	0.0	4.8	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	5.2	23.7	79.6	8.5
A	2	200592	1	0.0	0.0	0.4	0.0	0.0	0.0	0.0	3.1	0.0	0.0	0.0	2.1	5.5	91.6	1.4
	3	200592	1	0.0	0.0	0.7	0.0	0.0	0.0	0.0	11.6	0.7	1.2	0.0	0.2	1.2	54.5	0.0
A	4	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.6	0.0	0.0	0.0	1.7	6.3	112.3	0.0
Å	5	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.3	1.8	39.9	244.1	8.6
A	6	200592	1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.1	1.1	46.4	303.5	13.1
A	1	270592	14	0.0	0.0	0.7	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.4	0.4	14.2	169.8	2.0
A	2	270592	14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4	0.0	0.0	0.0	1.7	1.1	153.2	4.4
A	3	270592	14	0.0	0.0	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	25.3	84.0	0.0
A	4	270592	14	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.8	4.4	14.5	3.1
A	5	270592	14	0.0	0.0	0.7	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.1	0.0	10.7	91.4	0.0
A	6	270592	14	0.0	0.0	0.8	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.9	0.0	13.2	154.8	1.9
A	1	100692	28	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.1	2.4	158.5	1.8
٨	2	100692	28	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	3.5	231.5	2.3
A	3	100692	28	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.2	0.0	2.6	257.4	0.6
A	4	100692	28	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.4	0.0	1.9	147.7	1.0
٨	5	100692	28	0.0	0.0	0.0	0.0	0.3	0.0	0.0	1.9	0.0	0.0	0.0	0.0	3.5	273.5	0.7
A	6	100692	28	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.2	4.3	270.3	0.9
٨	1	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	29.7	0.0	0.0	0.7	11.3	23.9	160.4	137.4
٨	2	80792	56	0.0	6.0	0.0	0.0	0.0	0.0	0.0	37.4	0.0	0.0	0.4	40.6	15.2	245.8	179.0
	3	80792	56	0.0	0.0	0.4	0.0	0.0	0.0	0.0	22.3	0.0	0.0	1.2	22.1	19.0	149.6	115.5
٨	4	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	18.0	0.0	0.0	0.0	30.0	26.9	165.9	127.5
٨	5	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	18.4	0.0	0.0	24.2	23.8	126.1	110.4
A	6	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	46.2	0.0	0.0	1.4	53.8	30.2	163.0	219.2
A	1	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	1.0	0.0	0.3	17.1	2.4
	2	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5	0.0	0.0	1.0	0.0	0.0	80.9	1.3
A	3	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.1	0.0	0.0	63.3	1.9
٨	4	20992	112	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.5	0.0	0.1	64.2	3.1
A	5	20992	112	0.0	0.3	0.0	0.0	0.0	0.4	0.0	0.8	0.2	0.0	0.4	0.0	0.0	95.1	0.4
	6	20992	112	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.8	0.0	0.0	45.3	1.2

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Ţ	P	DATUM	TAG	COLNI	cocre	DICPU	LAGGE	00520	PLALA	SCARC	SCARM	SCART	SCELL	SCOSL	SCSEM	TECAU	TEKON	CHLUN
A	1	120592	0	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.2	0.0	0.3	0.0
٨	2	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A	3	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A	4	130532	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A	5	130532	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.4	0.0	0.0	0.0
A	6	130592	0	0.0	0.0	0.1	0.0	0.0	0.1	0.3	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.3
Å	1	200592	1	0.0	0.0	3.7	0.0	0.0	2.5	0.0	4.1	3.1	1.3	0.0	1.2	0.0	0.0	0.0
A	2	200592	1	0.0	0.0	6.9	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.2	0.0
٨	3	200592	1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	3.2	0.0	0.0	0.0	0.9	0.0
٨	4	200592	1	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5	0.0	0.5	0.0	0.0	0.0
A	5	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.3	1.8	0.0	0.9	0.0	0.0	0.0
A	6	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	2.3	0.0	0.0	0.0	0.0	0.0
٨	1	270592	14	0.0	0.0	0.0	0.1	0.0	0.0	0.0	2.0	1.3	0.0	0.0	0.7	0.0	0.0	0.0
4	2	210592	14	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.2	0.0
A		270592	14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.8	5.6	35.8	0.0	11.7	0.0	0.0	0.0
A	4	270592	14	0.3	0.0	0.0	0.0	0.0	0.0	G.4	0.0	0.0	1.5	0.0	0.6	0.0	0.0	0.0
٨	5	270592	14	0.2	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0
٨	6	270592	14	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.4
٨	1	100532	28	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.3	0.0
٨	2	100692	23	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.4	0.0	0.0	0.0
٨	170	100692	25	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
A	4	100632	25	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0
A	5	130592	28	0.0	6.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
٨	6	100692	28	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0 0	0.0	0.0	0.0	0.0	0.0	0.2
1	1	80792	55	0.0	0.0	0.7	0.0	0.0	0.0	0.0	1.2	0.0	0.0	3.0	0.0	0.0	0.8	0.0
Á	2	83792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.0	1.4	0.0	0.0	0.0	0.0	0.0	0.0
1	3	80792	Só	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0
A	1	80732	56	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.8	0.0	0.4	0.0	0.0	0.0	0.0	0.0
٨	5	80732	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.8	0.0	0.0	0.0	0.0	0.0
¥	5	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.2	0.0	0.6	0.0	0.4	0.0	0.0	0.0
٨	1	20335	112	0.4	0.0	0.0	0 .	0.0	0.0	0.0	0.0	0.4	0.2	0.0	0.0	0.0	0.0	0.0
7	2	23992		0.0	0.0	0.2	6.7	0.0	0.6	0.0	0.2	0.0	0.4	0.0	0.0	0.0	0.0	0.0
Å	3	20932		0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.4	0.1	0.2	0.0	0.0	0.0	0.0	0.0
A	1	20992		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.2	1.2	0.0	0.0	0.7	0.0	0.0
٨	5	20992		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	0.3
٨	5	20992	112	0.1	0.0	0 3	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0

in a contract of

T	P	DATUM	TAG	CSEHR	CSLUR	CSPRI	CSPRO	COLAE	COMEN	CJUND	CYARO	DIATO	EUGLE	CRYPT	CHLOR	CCZJU	ALGEN
A	1	130592	0	2.1	0.0	0.0	0.0	4.0	1.4	0.0	0.2	1.1	6.2	43.8	0.9	14.1	66.3
t.	2	130592	0	2.5	0.0	0.0	1.1	3.1	5.2	0.3	0.2	2.1	4.1	46.1	0.1	12.8	65.0
Á	3	130592	0	3.9	0.0	0.0	0.0	4.0	8.2	0.0	0.1	1.1	8.2	54.9	0.0	16.1	80.6
A	4	130592	0	2.0	0.0	0.0	0.0	3.4	1.0	0.0	0.0	1.0	6.1	55.3	0.1	12.4	15.5
A	5	130592	0	11.4	0.0	0.0	0.0	8.5	30.7	0.2	0.0	0.1	0.0	63.9	0.5	50.8	115.9
Á	6	130592	0	5.6	0.0	0.0	0.0	9.6	19.4	0.0	0.1	0.8	5.8	80.9	1.0	34.6	123.2
A	1	200592	1	93.6	0.0	13.3	0.0	134.3	411.1	0.0	73.3	132.8	0.7	117.0	22.0	652.3	998.1
Å	2	200592	1	6.6	0.0	0.0	0.0	1.1	22.1	0.0	12.2	1.1	3.1	103.6	1.2	37.0	158.4
A	3	200592	1	37.4	0.0	0.0	0.0	45.7	146.9	0.2	11.6	8.8	13.5	57.9	5.2	230.2	327.2
A	4	200592	1	1.0	0.0	0.0	0.0	5.8	26.1	0.0	6.1	1.2	12.6	120.3	2.5	32.9	176.2
A	5	200592	1	10.8	0.0	0.3	0.0	11.3	42.8	0.0	8.3	1.3	2.3	294.4	3.5	65.2	381.0
Á	6	200592	1	6.5	0.0	0.0	0.0	2.3	22.3	0.0	1.6	2.9	1.3	364.7	3.0	31.1	410.6
A	1	270592	14	49.7	0.0	1.3	0.0	49.3	161.8	0.0	21.8	5.1	1.5	186.4	4.1	262.1	481.6
A	2	270592	14	0.0	0.0	0.0	0.0	9.3	24.6	0.0	11.5	1.2	2.4	167.0	1.1	39.9	223.1
A	3	270592	14	174.3	0.0	1.4	0.0	410.4	1247.7	0.0	137.8	40.8	0.0	109.3	59.9	1839.8	2187.6
A	4	270592	14	19.9	0.0	0.6	0.0	12.1	168.1	0.0	11.6	1.3	0.6	83.4	2.9	200.7	302.5
A	5	270592	14	22.9	0.0	0.2	0.0	11.9	169.9	0.0	15.6	8.7	1.1	102.1	2.4	204.9	335.8
A	6	270592	14	10.9	0.0	0.0	0.0	16.5	80.6	0.0	3.2	6.1	1.9	179.9	1.8	108.0	300.5
A	1	100692	28	5.7	0.0	0.0	0.0	8.1	21.7	0.0	18.3	1.3	0.4	162.8	0.9	35.5	225.2
A	2	100692	28	0.5	0.0	0.3	0.0	1.5	14.7	0.0	1.9	1.5	0.4	237.3	0.8	17.0	258.5
A	3	100692	26	5.6	٥, ٥	1.1	0.0	1.3	47.3	0.0	9.6	2.1	1.1	260.6	1.1	55.3	330.
A	4	100692	28	0.4	0.0	0.0	0.0	2.2	15.7	0.0	2.5	1.6	1.1	150.5	0.4	18.3	174.
A	5	100692	28	1.9	0.0	6.0	0.0	1 0	43.3	0.0	8.6	2.9	1.9	211.1	1.0	46.2	338.3
A	6	100592	28	1.5	0.0	0.0	0.0	0.2	32.1	0.6	1.7	3.1	1.5	275.7	0.2	33.8	316.
A	1	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.8	30.4	333.0	2.1	0.0	370.
A	2	80792	56	0.0	0.0	0.0	0.0	0.6	0.0	0.0	1.0	23.4	37.8	480.6	6.4	0.6	549.
A	3	80792	56	0.0	0.0	6.0	0.0	0.0	0.0	0.0	0.0	9.0	23.5	307.2	1.4	0.0	341.
A	4	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.1	18.0	350.3	2.0	0.0	382.
A	5	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.2	18.4	284.5	1.4	0.0	314.
A	6	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	13.4	47.6	526.2	3.2	0.0	590.
	1	20992	112	0.0	0.0	0.0	0.0	0.1	0.6	0.0	0.0	0.7	2.0	79.8	1.0	0.7	84.
A	2	20992	112	0.5	0.0	0.0	0.0	0.0	0.2	0.0	0.0	1.0	2.5	82.2	0.8	0.7	87.
A	3	20992	112	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.2	1.0	0.6	65.2	0.8	0.8	68.
A	4	20992	112	1.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	2.0	1.3	67.4	1.9	1.3	13.
A	5	20992	112	0.8	0.0	0.1	0.0	0.1	0.4	0.0	0.1	1.5	1.4	95.5	1.2	1.4	101.
A	6	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	1.5	46.5	0.9	0.0	49.

Mr. arabitration

ī	1	DATUM	TAG	COEKU	PSAAR	ACNOR	AMPPS	AULIT	CALBA	CYCNE	CYNVE	31H10	DITEN	DIVUL	FRACR	GONSP	MACUS	NASU3-	MASPE
8		130592	. 0	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
8		130592	0	0.0	0.0	0.0	0.9	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
6		130532	0	0.0	3.1	0.7	0.0	0.0	0.3	2.1	0.0	0.0	0.0	0.0	8.0	0.0	0.5	0.0	0.0
8		130592	. 0	0.0	1.0	0.3	0.0	0.3	1.5	0.9	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
8	1	130593	0	0.0	9.7	3.0	0.0	1.5	6.0	6.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0
8	1	130592	0	0.0	2.0	0.9	1.0	1.5	0.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0
8		200592	1	0.0	20.3	5.6	0.0	2.8	0.0	12.2	0.0	0.0	0.0	0.0	2.8	0.0	0.0	0.0	0.0
8	1	200532	1	0.0	2.0	0.3	0.0	0.3	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1	200592	1	0.0	29.3	4.2	0.0	5.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8		200592	1	0.0	6.3	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8		200542	1	0.0	8.3	4.6	0.0	0.0	0.5	1.4	0.0	0.0	3.2	0.0	0.0	0.0	0.0	0.0	0.0
8	1	200590		0.0	1.5	2.3	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8		270532	14	0.0	1.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	0.0	0.0	0.0	0.0
8	1	270592	14	0.0	5.9	0.6	0.0	0.4	0.0	2.0	0.9	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0
8		270592	14	0.0	182.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1	270592	14	0.0	13.9	4.2	0.0	0.5	0.6	1.2	0.0	0.0	9.2	0.0	0.0	0.0	0.0	0.0	0.0
8		270592	14	2.2	67.8	2.2	0.0	6.7	0.0	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	1	270592	14	0.0	9.3	2.2	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8		100593	23	0.0	6.0	G.8	0.0	0.7	0.0	0.7	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0
9	1	100632	28	0.0	3.5	0.2	0.0	0.0	0.0	2.1	0.0	0.2	0.0	0.0	0.9	.0	0.0	0.0	0.0
3		100592	23	0.0	0.0	0.0	0.0	3.4	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	ũ.2	0.0	0.0
8		100593	28	0.7	12.0	0.0	0.0	4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1	100693	23	0.6	10.2	0.0	0.0	2.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0
8		100592	28	0.0	4.9	0.0	0.0	2.3	0.0	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8			-	0.0	1.5	0.1	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9	- 3			0.0	0.8	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9				0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3				0.0	0.9	0.0	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1	80793	56	0.0	1.4	0.1	0.0	0.0	0.0	3.1	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0
8	1			0.0	1.1	0.0	0.0	0.0	0.9	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	3	20993	112	0.0	0.0	0.4	0.0	0.0	0.0	1.4	0.0	0.0	*	0.0	0.0	0.0	0.0	0.0	0.0
8		20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0 0	0.0	0.0	0.0	0.0	0.0
3				0.0	0.0	0.4	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3		20993		0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1			0.0	0.0	0.5	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	1	20993	112	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	1.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0

sicurationes

T	1	MIL.YC	TAG	MICAP	MIFON	MISUA	STANC	SYNAC	OLUND	EUSPC	PHOSE	PHPLE	PHPYR	TRSPC	CRERC	CRMAR	CHNCR	RHOLA
8	1	130592	0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	1.2	0.5	0.0	0.0	3.0	23.9	95.9	0.0
8	2	130592	0	0.0	0.8	0.0	0.0	0.0	0.0	0.0	5.5	1.1	0.0	0.9	1.0	20.5	85.0	0.0
8	3	130592	0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	1.8	0.0	0.0	0.0	0.4	15.7	125.0	1.8
8	4	130592	0	0.3	0.0	0.5	0.0	0.0	0.0	0.0	2.2	0.0	0.0	0.0	3.2	24.3	84.2	0.0
8	5	130592	0	0.0	0.0	0.4	0.4	0.0	0.2	0.0	1.5	0.0	0.0	0.0	0.2	19.5	107.7	2.6
8	6	130592	0	0.1	0.0	0.3	0.0	0.0	0.0	0.0	3.3	0.0	0.0	0.0	1.0	11.3	12.5	0.0
8	1	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	1.4	40.6	134.0	4.2
8	2	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5	0.0	0.0	0.1	0.7	43.8	212.5	1.3
8	3	200592	1	0.0	0.0	4.9	0.0	0.0	0.0	0.0	2.2	0.0	0.0	0.0	0.9	23.1	65.0	0.0
8	4	200592	1	0.0	0.0	1.1	0.0	0.0	0.3	0.0	1.4	0.0	0.0	0.0	1.4	67.3	242.9	0.0
8	5	200592	1	0.0	0.0	1.2	0.0	0.9	0.0	0.0	15.7	0.0	0.5	0.0	3.1	24.0	194.0	4.5
8	6	200592	1	0.4	0.0	0.4	0.0	0.0	0.0	0.0	11.1	0.0	0.0	0.0	11.3	41.5	257.5	0.0
8	1	270592	14	0.0	0.0	2.3	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.9	6.4	146.5	0.5
8	2	270592	14	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.5	1.1	79.9	2.6
8	3	270592	14	0.0	0.0	60.0	0.0	0.0	0.0	0.0	2.2	0.0	0.0	0.0	0.0	17.8	93.3	4.4
В	4	270592	14	0.0	0.0	3.1	6.0	0.0	0.0	0.0	6.1	0.0	0.0	0.0	0.6	1.8	112.0	11.7
8	5	270592	14	0.0	0.0	4.4	0.0	0.0	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.0	25.5	3.3
8	6	270592	14	0.0	0.0	3.1	0.0	0.0	0.0	0.0	5.1	0.0	0.0	0.0	4.2	12.4	13.9	1.1
8	1	100592	28	0.0	0.0	0.4	0.0	0.2	0.0	0.0	2.2	0.0	0.0	0 1	2.7	3.1	335.3	11.1
8	2	100592	28	0.0	0.0	0.5	0.0	0.0	0.0	0.0	4.1	0.0	0.0	0.0	1.5	6.8	234.4	4.9
8	3	100592	25	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	6.6	1.1	135.9	0.0
8	4	100532	28	0.9	0.0	2.6	0.0	0.0	0.1	0.0	2.3	0.0	0.0	0.0	0.9	1.9	143.4	0.0
8	5	100632	23	0.0	0.3	1.2	0.0	0.0	0.0	0.0	5.8	0.0	0.0	0.0	3.2	19.5	343.1	0.0
8	6	100532	28	0.0	0.0	0.9	0.0	0.0	0.0	0.0	2.6	0.0	0.0	0.0	9.0	10.5	245.9	0.0
8	1	80792	55	0.0	0.0	0.0	0.0	0.0	0.0	0.0	14.7	0.0	0.0	2.0	10.8	12.7	343.7	57.1
8	2	80792	56	0.0	0.0	0.2	0.0	0.0	0.0	0.0	15.7	0.0	0.0	1.5	4.5	30.7	306.4	20.2
8	3	80792	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.4	0.0	0.0	3.0	1.9	21.0	259.0	31.5
3	4	80792	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.2	0.9	0.0	2.3	6.9	22.0	343.0	38.1
9	5	80792	56	0.0	0.0	0.0	0.0	0.0	0.1	0.0	11.1	0.0	0.0	0.7	4.1	5.8	301.4	47.4
8	6	80792		0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	3.5	2.4	14.6	159.1	23.5
8	1	20992	112	0.0	0.1	0.0	0.0	0.0	0.0	0.0	1.1	0.5	0.0	1.6	3.0	4.5	142.5	10.4
3	2	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.8	0.5	0.0	1.0	1.3	2.5	170.9	15.4
8	3	20392	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.1	0.0	0.0	1.3	0.7	4.0	139.4	9.7
8	1	20992	112	0.0	0.8	0.0	0.0	0.0	0.3	0.0	3.7	0.0	0.0	1.1	1.1	3.1	145.3	25.6
8	5	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.8	0.2	0.0	0.9	0.9	2.5	45.9	27.8
8	6	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.7	0.0	0.0	0.0	3.1	1.5	145.2	20.4

material regions

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T	9	MUTAD	TAG	COLNI	COCFO	DECPU	LAGGE	OOSPC	PLALA	SCARC	SCARN	SCART	SCELL	SCO3L	SCSEN	TECAU	TECON	CHLUN
8	1	130592	0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	2	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	3	130592	0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0
8	4	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.0	0.0	0.0	0.0	0.0	0.0
8		130592	0	0.0	0.6	0.4	0.0	0.0	0.0	2.2	0.0	0.0	2.2	0.0	1.1	0.0	0.0	0.0
8		130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	U.0	0.5	0.0	0.0	0.0	0.0	0.0
8		200592	1	0.0	0.0	0.3	0.0	0.0	1.7	0.0	0.0	1.9	1.4	0.0	3.1	0.0	0.0	0.8
3		200532	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.8
8		200592	1	0.4	0.0	0.9	0.0	0.0	0.0	0.0	3.3	0.0	2.2	0.0	0.0	0.0	0.4	0.7
8		200532	1	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	1.5	0.0	C.0	0.0	0.0	0.8
8	5	200592	1	0.0	0.0	0.5	0.0	0.0	0.0	0.0	1.4	0.0	0.9	0.0	0.0	0.0	1.8	0.0
8	6	200532	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1	212592	14	0.0	0.0	0.1	0.0	0.0	0.0	0.5	0.0	0.1	1.0	0.0	0.4	0.0	0.0	0.0
8	2	277592	14	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	3	270592	14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	17.8	0.0	0.0	0.0	6.1	0.0	0.0	0.0
8	4	270592	14	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.8	0.0	0.0	0.0
8	5	270592	14	0.0	1.1	1.8	0.0	0.0	0.0	0.0	2.2	2.2	12.2	0.0	0.0	0.0	0.0	0.0
8	6	210592	14	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.4
8	1	100532	28	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
6	2	100592	28	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.4
8	3	100592	28	0.0	0.0	0.8	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0
8	4	102592	23	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	3	100652	23	0.3	0.0	0.3	0.0	0.0	2.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
8	6	100532	25	0.0	0.0	0.2	0.0	3.0	0.2	0.0	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.0
8	1	82792	56	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	2	80792	55	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0
3	3	80732	53	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	4	89792	.6	0.0	0.0	0.5	0.0	0.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
E	5	80792	56	0.0	0.0	0.1	0.0	0.0	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	6	80792	56	0.0	0.0	0.2	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
8	2	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	3	2093	1	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0
3	4	20992	19	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	0.2
ī	5		1.7	0.0	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0	1.1	0.0	0.5	0.0	0.0	0.0
8	6	20992	112	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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Ţ	P	CATUM	TAG	CSESS	CSLUN	CSPRI	CSPRO	COLAE	COMEN	CTANO	CYANO	OTATO	EUGLE	CRYPT	CHLOR	CONJU	AL.
3	1	130592	0	3.8	0.0	0.0	0.0	5.3	6.3	0.0	0.0	1.9	1.2	123.5	0.1	15.4	14
8	2	130592	0	3.3	0.0	0.0	0.0	3.8	6.1	0.0	0.0	1.4	6.1	107.5	0.0	13.8	12
8	3	130592	0	25.0	0.0	0.6	0.0	14.6	8.4	0.0	3.1	5.5	1.3	143.9	0.8	48.6	20
8	4	130592	0	2.4	0.0	0.4	0.0	5.1	7.5	0.0	1.0	3.1	2.2	111.7	0.4	15.7	13
8	5	130592	0	29.4	0.0	3.5	0.0	23.2	65.8	0.0	9.7	12.1	1.5	130.0	6.5	127.9	28
8	6	130532	0	7.9	0.0	0.4	0.0	9.9	18.4	0.0	2.0	4.1	3.9	84.8	0.5	35.6	13
8	1	200592	1	48.9	0.0	5.8	0.0	30.6	111.5	0.0	29.3	23.4	0.3	230.2	9.2	196.8	48
8	2	200592	1	2.4	0.0	0.0	0.0	2.1	5.6	0.0	2.0	1.4	5.1	253.3	1.6	10.1	23
8	3	200592	1	183.6	0.0	17.8	0.0	129.4	257.1	1.8	23.3	14.9	2.2	83.0	1.9	539.7	13
3	4	200592	1	16.1	0.0	0.0	0.0	6.1	58.9	0.0	6.3	1.2	1.4	313.5	2.4	81.1	4:
8	5	200592	1	85.5	0.0	0.9	0.0	16.2	231.0	3.7	8.3	13.8	16.2	226.3	4.6	337.3	60
9	6	200592	1	5.5	0.0	0.5	0.0	9.7	11.1	0.0	3.5	3.5	11.1	320.5	0.0	33.8	37.
8	1	270592	14	21.3	0.0	0.1	0.0	10.0	99.5	0.0	1.1	6.4	1.1	154.3	2.1	130.9	300
8	2	270592	14	5.9	0.0	0.3	0.0	1.0	42.6	0.0	5.9	4.5	0.4	84.7	0.2	56.8	150
8	3	270592	14	222.2	0.0	17.8	0.0	455.6	1139.9	0.0	182.2	60.0	2.2	115.5	24.5	1846.5	2231
8	4	270592	14	27.8	0.0	2.8	0.0	1.5	129.3	0.0	13.9	18.9	6.1	132.1	2.0	167.4	340
8	5	270592	14	240.2	0.0	31.1	0.0	195.7	934.1	0.0	70.0	15.5	3.3	23.9	25.5	1451.1	159-
3	6	270532	14	10.4	0.0	0.0	0.0	22.0	19.1	0.0	9.3	1.1	5.1	91.6	0.8	112.1	22:
8	1	100592	25	13.5	0.0	1.3	0.0	2.9	63.3	0.0	6.0	3.5	2.2	353.2	0.2	81.0	445
8	2	1 0692	28	12.2	0.0	0.2	0.0	1.1	42.2	0.0	3.5	4.0	4.1	237.6	0.3	55.7	165
ŝ	3	100592	23	31.4	0.5	0.1	2.8	15.0	64.9	0.1	0.0	6.1	0.4	151.2	1.5	115.4	27:
3	4	100532	28	32.0	0.0	1.9	0.0	19.3	94.2	0.0	12.7	9.1	2.3	152.2	0.0	147.4	320
8	5	100532	28	12.5	0.0	1.2	0.0	13.1	200.6	0.5	10.8	4.1	5.8	355.5	4.1	223.1	620
8	6	100592	23	9.4	0.0	0.2	0.0	11.1	61.4	0.0	4.3	3.2	2.5	255.4	0.8	85.1	352
8	1	80792	55	0.0	0.1	0.0	0.0	0.1	0.0	0.0	1.8	0.7	15.7	430.3	0.3	0.1	443
3	2	80792	56	1.3	0.0	0.0	0.0	0.0	1.0	0.0	0.8	0.8	17.2	351.9	0.2	2.3	333
8	3	80792	56	0.2	0.0	0.0	0.0	0.3	0.5	0.0	0.0	0.6	11.4	319.4	0.3	1.1	332
3	4	80192	55	1.0	0.0	0.0	0.0	0.3	0.0	0.0	0.8	1.5	23.5	410.0	2.0	1.3	439
8	5	80192	56	1.7	0.0	0.1	0.0	0.0	0.0	0.0	1.4	3.6	11.8	359.3	2.1	1.8	390
8	6	80792	55	0.4	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.7	10.5	205.4	1.9	0.4	220
8	1	20992	112	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1	97.8	160.5	1.0	1.0	174
8	2	20392	112	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	1.3	191.5	0.0	0.0	199
8	3	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	8.0	153.8	0.7	0.0	16:
3	4	20992	112	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7	4.8	177.1	1.5	1,1	135
3	5	20992	112	1.5	0.0	0.0	0.0	0.0	1.5	0.0	0.0	1.0	4.9	78.1	3.8	3.0	90
8	6	20992	112	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5	5.1	171.1	0.8	0.3	179

Harman Harman

í		DATUM	TAC	COEKU	PSAAR	ACMOR	AMPPS	AULIT	CALSA	CYCNE	CANAE	31810	DITEN	3 C 1 C 5 C	-	SCMSP	MACUS	NASU8	NASP
C		130592	0	0.0	0.4	0.8	0.2	0.1	0.6	1.5	0.1	0.0	0.0	0.0	0.2	0.0	0.8	0.0	٥.
C		130592	0	0.0	0.4	0.0	0.0	1.2	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.
C	-	130592	0	0.0	0.0	0.3	0.0	0.7	0.2	0.9	0.0	0.0	0.0	0.0	8.0	0.0	0.1	0.4	0.
C	4	130592	0	0.0	0.0	0.0	0.0	0.6	0.0	1.4	0.0	0.0	0.0	0.0	0.5	0.0	0.6	0.0	0.
C	5	130592	0	0.0	0.0	0.0	0.0	1.7	0.0	0.2	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.1	0.
C	6	130532	0	0.0	0.3	0.3	0.0	0.5	0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.
C	1	200532	1	0.0	3.2	8.0	0.0	0.0	0.0	1.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.
C	2	200592	1	0.0	1.6	6.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.
C	3	200592	1	0.0	12.0	0.7	0.0	1.5	0.0	0.3	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.1
C	4	200592	1	0.0	1.3	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	5	200592	1	0.0	12.2	1.1	0.0	9.3	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0
C	6	200592	1	0.8	2.5	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	1	270592	14	0.0	6.9	0.9	0.0	0.0	1.8	2.3	0.0	0.0	12.5	0.0	0.0	0.0	0.0	0.0	0.0
C	2	270592	14	0.0	1.4	0.6	0.0	0.6	0.0	0.9	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	3	270592	14	0.0	25.5	10.6	0.0	0.0	1.7	1.7	0.0	0.0	14.5	0.0	0.0	0.0	0.0	0.0	0.0
C	4	270592	14	0.0	4.5	1.3	0.0	0.0	0.5	2.1	0.0	0.0	0.0	2.1	0.3	0.0	0.0	0.0	0.0
C	5	270592	14	0.0	17.5	0.5	0.0	2.5	0.3	0.0	0.0	0.0	0.0	8.0	0.0	0.0	0.0	0.0	0.0
C	5	270592	14	0.7	5.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.0
C	1	100532	23	0.0	2.5	1.5	0.0	0.0	0.0	2.1	0.0	0.0	2.5	1.6	0.0	0.0	3.0	0.0	0.0
C	2	190592	23	0.0	2.4	0.0	0.0	0.0	0.4	4.9	0.0	0.0	0.0	0.0	0.0	.0	0.0	0.0	0.3
C	3	100592	25	0.9	1.1	2.8	0.0	0.0	0.0	4.5	0.9	0.0	6.1	0.0	0.0	0.0	0.0	0.0	0.0
C	4	100632	28	0.5	2.3	0.0	0.0	0.0	0.5	0.7	0.0	0.0	3.5	0.0	0.0		0.0	0.0	0.0
C	5	100592	23	0.0	19.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.1	0.0	0.0	0.0	1.3	0.0	0.0
C	8	100592	28	0.0	3.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.2	0.0	0.0	0 1	0.2	0.0	0.0
C	1	40531	55	0.0	0.0	0.0	0.9	0.0	0.0	3.4	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0
C	2	110631	56	0.0	6.2	0.0	0.0	0.0	0.7	5.3	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0
C	1	240431	56	0.0	4.5	0.0	0.0	0.0	0.0	5.5	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0	0.0
C	4	140591	55	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
C	5	170591	55	0.0	2.9	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	6	210591	55	0.0	4.2	0.0	0.0	0.0	0.0	1.4	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0
C	1	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	9.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	2	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	3	29332	112	0.0	0.0	0.0	0.0	0.0	0.0	13.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
¢	4	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	7.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	5	20992	1:2	0.0	0.0	0.0	0.0	0.0	0.5	10.6	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.1	0.0
C	6	20992	112	0.0	0.0	0.0	0.0	0.0	1.3	9.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

1	P	DATUM	Tág	MICAP	MIFON	MISUA	STANC	SYNAC	CRUIO	EUSPC	PHOSC	PHPLE	PHPYR	TRSPC	CRERO	CRMAR	CHMOR	RHOLA
C	1	130592	0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	2.9	0.0	0.0	0.0	0.5	13.4	61.6	0.1
C	2	130592	0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	5.8	0.0	0.0	0.2	1.2	13.3	53.9	0.0
C	3	130592	0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	2.8	3.0	0.0	0.0	0.9	17.3	70.8	0.0
C	4	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.3	0.0	0.0	0.0	1.5	13.1	51 5	0.5
C	5	130592	0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	2.6	0.1	0.0	0.0	0.0	8.2	63.0	0.3
C	6	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4	0.0	0.0	0.0	0.6	10.3	51.2	0.0
C	1	200592	1	0.0	0.0	0.0	0.0	J.0	0.0	0.0	7.1	0.0	0.0	0.0	0.6	5.0	90.5	0.0
C	2	200:32	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	25.5	0.0	0.0	0.0	2.4	5.8	131.1	0.0
C	3	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8	0.0	0.0	0.0	3.2	31.4	225.3	15.8
C	4	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.3	0.0	0.0	0.0	9.0	30.1	215.2	11.4
C		200592	1	0.0	0.0	1.1	0.0	0.0	0.0	0.0	14.4	0.0	0.0	0.0	25.7	18.4	193.1	0.0
C	6	200532	1	0.0	6.0	0.8	0.0	0.0	0.0	0.0	14.1	0.0	0.0	0.0	4.5	41.3	159.1	0.0
C	1	270532	14	0.0	0.0	5.1	0.0	0.0	0.0	0.0	3.2	0.0	0.0	0.0	0.0	14.8	21.3	18.0
C	2	270592	14	1.2	0.0	2.5	0.0	0.0	0.0	0.0	1.4	0.0	0.0	0.0	1.2	31.4	37.0	12.5
C		270532	14	0.0	0.0	2.8	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	15.0	45.1	13.3
C	4	270592	11	0.0	0.0	1.5	0.0	0.0	0.0	0.0	15.3	0.0	0.0	0.0	4.5	25.9	51.4	17.2
C	5	270592	14	9.9	0.0	1.2	0.0	0.0	0.0	0.0	3.1	0.0	0.9	0.0	4.9	25.5	57.0	1.1
C		210592	14	0.3	0.0	1.7	0.0	0.0	0.0	0.0	17.1	0.0	0.0	0.0	5.4	23.5	53.2	13.4
C		100532	23	0.9	0.0	1.4	0.0	0.0	2.1	0.0	9.0	0.0	0.0	0.0	10.2	12.5	237.4	0.0
C		100532	25	1.3	0.0	1.7	0.0	0.9	0.0	0.0	8.1	0.0	0.0	0.0	9.2	41.1	295.0	0.0
C		100532	23	0.0	0.0	2.5	0.0	0.0	0.0	0.0	5.0	0.0	0.0	0.0	4.2	38.1	253.8	0.0
C		100532	23	0.7	0.0	0.0	0.0	0 0	0.0	0.0	10.7	0.0	0.0	0.0	1.2	25.0	251.2	0.0
C		100592	23	0.0	0.0	8.2	0.0	0.0	0.0	0.0	6.7	0.0	0.0	0.0	7.1	15.9	435.7	0.0
C	ó	100692	23	0.0	0.0	1.8	0.0	0.0	2.2	0.0	9.1	0.0	0.0	0.0	10.3	34.2	437.1	0.0
C	1	42691	55	0.0	0.0	0.5	0.0	0.0	0.5	0.0	2.6	0.0	0.0	0.0	2.0	5.8	122.8	0.5
C	2	110631	55	0.0	0.0	0.4	0.0	0.0	0.0	0.0	1.8	0.0	0.0	0.9	0.7	8.8	0.0	9.9
C	3	540431	55	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.3	4.9	221.2	0.0
C	4	140591	55	0.0	0.0	0.5	0.0	0.0	0.0	0.0	2.3	0.0	0.0	0.2	0.3	4.8	183.3	1.3
C	5	170591	55	0.0	0.0	u.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.7	4.7	1.1	151.0	2.1
C	6	210591	55	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.4	0.0	0.0	0.5	2.0	2.6	113.1	1.5
C	1	29992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.0	15.8	9.3	12.0	11.4	21.5
C	2	10 H / H / H / H / H		0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	31.5	1.6	11.0	64.3	20.4
C	3	21992	112	0.0	0.0	0.0	9.0	0.0	0.0	0.0	1.9	0.0	0.0	25.5	4.9	4.1	18.5	24.9
Ç	4	20992		0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.2	0.0	0.0	31.5	5.7	1.4	37.5	21.8
C	5	20932	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.5	0.0	0.0	18.0	4.7	5.4	16.5	18.7
C	6	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	17.4	5.0	4.9	15.4	19.5

HABOURDERS.

T	P	DATUM	TAG	COLMI	COCFO	נייסוס	LAGGE	00520	PLALA	SCARC	SCARM	SCART	SCELL	SCOBL	SCSEM	TECAU	TEKON	CHLUN
C	1	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	3.0	0.4	0.0	0.0	0.0
C	2	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	3	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	4	120532	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	5	130592	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	6	130592	0	0.0	0.0	0 0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
C	1	200592	1	0.4	0.0	6.4	0.0	1.0	0.0	0.0	0.0	0.0	6.1	0.0	0.0	0.0	0.0	0.0
C	2	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0_0	0.0	0.0	1.5	0.0	0.0	0.0	0.3	0.0
C	3	200592	1	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.6	1.0	0.1	0.0	0.0	0.0
C	4	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1 0	0.6	0.0	0.0	0.0	0.0	0.0	0.0
C	5	200532	1	0.0	0.0	3.0	0.0	0.0	0.0	0.0		0.0	5.5	0.0	1.1	0.0	0.0	0.0
C	6	200592	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0		1.0	0.0	0.0	0.0	0.0	0.3	1.0
C	1	210592	14	0.0	0.0	0.0	0.0	0.0	8.8	0.0	0	6.0	5.9	0.0	0.0	0.0	0.0	1.8
C	2	270592	14	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0	1.2	1.8	0.0	0.0	0.0	1.5	3.4
C	3	210592	14	0.0	0.0	0.0	0.0	0.0	12.8	0.0	0.0	5.1	1.7	0.0	0.0	0.0	0.0	3.3
C	4	270592	14	0.0	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.3	1.1	0.0	0.3	0.0	0.0	2.4
C	5	270592	14	0.0	0.0	0.6	- 0.0	0.0	0.5	0.0	0.0	0.9	2.2	0.0	0.0	0.0	0.0	0.3
C	6	270592	14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.1	1.3	2.0	0.0	0.0	0.0	0.7
C	1	100632	23	0.2	0.0	0.0	0.0	0.0	0.7	0.0	0.0	2.5	2.1	0.0	0.0	0.0	0.0	0.0
C	2	100632	29	0.0	0.0	0.0	0.0	0.0	0.4	0.0	1.3	0.9	0.0	0.0	0.0	0.0	0.0	0.0
C	3	100592	28	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0	2.8	4.4	0.3	0.0	0.0	0.0	0.5
C	4	100632	23	0.2	0.2	0.7	0.0	0.2	1.4	0.0	0.0	1.5	0.5	0.0	0.0	0.0	0.0	0.0
C	5	100532	23	1.3	0.0	0.0	0.0	0.0	0.9	0.9	0.0	3.5	2.5	1.3	0.4	0.4	0.0	0.0
C	ó	100692	23	0.0	0.4	0.0	0.0	0.0	9.2	0.0	0.0	1.1	1.5	0.0	0.0	0.0	0.0	0.0
C	1	40591	50	0.0	0.0	1.1	0.0	0.0	0.0	0.0	15.3	0.4	0.0	0.3	0.9	0.0	0.0	112.5
C	2	110631	56	0.7	0.0	0.2	0.0	0.0	0.0	0.4	8.4	0.4	0.7	0.0	0.0	0.0	1.1	0.9
C	3	540431	55	0.0	0.0	1.3	0.0	0.0	0.0	1.0	6.9	1.5	1.8	0.0	0.8	0.0	2.8	213.5
C	4	140591	56	0.3	0.0	0.3	0.0	0.7	0.0	1.5	4.5	1.3	1.0	0.0	0.5	0.0	0.5	129.0
C	5	170591	56	0.4	6.0	0.1	0.0	0.3	0.7	1.8	3.5	0.4	0.0	0.0	0.1	9.9	0.0	65.1
C	6	210591	55	0.6	0.0	0.0	0.0	0.0	0.4	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	1	20992	112	0.0	0.4	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0
C	2	20992	112	0.9	0.0	0.0	0.0	0.5	0.0	0.5	0.3	0.0	0.0	0.0	0.0	0.0	6.0	0.0
C	3	20932	112	0.0	0.1	0.0	C.0	0.3	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
C	4	20992		0.0	0.0	0.2	0.0	0.3	0.0	0.3	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0
C	5	20192		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	6	20992	112	G.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0

with the con-

T	P	DATUM	TAG	CSEMR	CSLUN	CSPRI	CSPRO	COLAE	COMEN	CJUND	CYANO	DIATO	EUGLE	CRYPT	CHLOR	CONJU	ALGEN
¢	1	130592	0	6.4	0.0	0.2	0.0	5.5	5.7	0.2	6.4	4.9	2.9	15.7	0.6	18.0	102.5
C		130592	0	1.9	0.0	0.0	0.0	6.5	1.4	0.0	0.4	4.2	6.0	68.4	0.0	17.8	95.8
Ç		130592	0	3.8	0.0	0.0	0.0	5.5	5.9	0.0	0.0	3.1	2.8	82.5	0.0	15.2	111.2
C	4	130592	0	2.8	0.0	0.0	9.0	5.0	2.6	0.0	0.0	3.1	2.3	69.7	0.0	10.4	85.5
C	855	130592	0	1.3	0.0	0.2	0.0	3.0	9.9	0.0	0.0	2.4	2.1	68.5	0.0	14.4	88.0
C		130592	0	2.1	0.6	0.4	0.0	2.5	8.4	0.0	0.3	1.4	2.4	65.1	0.2	13.4	82.8
C		200592	1	26.7	0.0	0.0	0.0	1.9	21.2	0.0	3.2	2.0	1.1	96.1	6.9	55.8	171.1
C		200592	1	6.4	0.0	0.0	0.0	4.0	7.8	0.0	1.0	0.3	25.5	132.3	1.8	18.2	185.1
C		200592	1	20.0	0.0	3.4	0.0	15.8	46.3	0.0	12.0	2.5	2.8	275.7	2.3	85.5	381.2
C	4	200592	1	4.4	0.0	0.0	0.0	2.2	1.8	0.0	1.3	1.3	3.3	258.5	0.6	11.4	276.4
C	5	200592	1	13.7	0.0	0.0	0.0	26.3	206.1	0.7	12.2	11.5	14.4	292.2	6.7	246.8	583.8
C	6	200592	1	5.3	0.0	0.0	0.0	9.3	24.2	0.0	3.3	1.3	14.1	214.9	1.3	38.8	213.1
C		270592	14	58.2	0.0	1.5	0.0	64.7	333.6	0.0	6.9	22.6	1.2	54.1	17.5	458.3	562.6
C		270592	14	19.1	0.0	3.1	0.0	8.3	116.4	0.0	3.4	5.8	1.4	82.2	8.5	146.9	254.2
C		270592	14	56.7	0.0	11.7	0.0	50.6	551.0	0.0	25.6	31.3	11	14.4	23.9	670.0	826.3
C		270592	14	1.9	0.0	0.5	0.0	12.9	99.5	0.0	4.5	1.9	15.3	102.0	5.2	120.8	255.7
C		210592	14	31.1	0.0	5.5	0.0	53.9	237.2	0.0	17.6	21.9	3.1	92.1	4.6	321.1	467.0
C		270592	14	20.2	0.0	0.0	0.0	5.0	146.2	0.0	6.4	4.7	17.1	110.6	5.4	171.4	315.6
C	1	100692	28	23.9	0.0	2.3	0.0	33.6	172.1	0.0	2.8	12.5	9.0	370.2	5.4	231.9	631.8
C	25	100692	28	4.1	0.0	1.5	0.0	8.8	26.5	0.0	2.4	8.3	8.1	345.9	2.6	40.9	409.2
C		100692	26	10.3	0.0	0.3	0.0	48.9	321.2	0.0	4.0	13.9	5.0	296.1	9.2	386.7	714.9
C		100692	28	3.9	0.0	0.5	1.0	6.3	58.5	0.2	2.8	5.4	10.7	295.4	4.8	69.4	388.5
C		100692	28	24.9	0.6	4.0	0.0	25.3	168.3	0.0	19.1	22.6	6.1	454.7	10.5	222.5	736.1
C	6	100592	28	12.0	0.0	0.9	0.0	11.5	17.9	0.0	3.6	14.4	9.1	482.2	1.5	102.3	\$15.1
C	1	40591	56	4.4	0.0	0.7	0.0	0.6	1.0	0.0	0.0	5.0	2.6	131.2	130.5	6.7	276.0
C		110691	56	6.3	0.0	0.0	0.0	0.5	0.5	0.0	6.2	1.5	2.1	19.4	12.8	1.3	55.9
C		240491	56	3.3	0.0	0.0	0.0	1.0	0.0	0.0	4.6	1.1	0.0	230.4	229.6	4.3	476.0
C		140591	56	1.3	0.0	0.0	0.0	1.0	0.2	0.0	0.0	1.5	2.5	189.7	139.6	2.5	335.8
C		170591	56	1.1	0.0	0.3	0.0	2.5	0.4	0.0	2.9	3.0	3.2	165.5	12.4	4.3	251.3
C	6	210591		4.4	0.0	0.0	0.0	2.0	0.5	0.0	4.2	1.9	4.9	130.3	8.2	6.9	162.4
C	1	50005		0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.9	16.4	119.2	2.1	0.4	148.0
C	2	: 212		0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3	34.1	103.3	1.5	0.6	145.8
C	3	20992		0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	13.9	27.5	52.4	0.7	0.8	95.3
C	4	20992	22	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	34.8	75.4	1.2	0.5	118.9
C	5	20992		1 4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.5	22.6	66.3	0.0	1.8	102.2
C	6	20992	112	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.3	17.9	15.9	0.4	0.0	104.5

BBMON

1. Cladocera

DAMAG = Daphnia magna

DALON = Daphnia longispina

CAJUV = juvenile Daphnia (überwiegend D. longispina)

SCMUC = Scapholeberis mucronata SIVET = Simocephalus vetulus BOLON = Bosmina longirostris

ALAF = Alona affinis

CHYSP = Chydorus sphaericus POPED = Polyphemus pediculus SUCLD = Summe der Cladocera

2. Copepoda

EUVUL = Eudiaptomus vulgaris CYSTR = Cyclops strenuus

EUSER = Eucyclops serrulatus

NAU = Nauplien COP = Copepodite

SUCOP = Summe der Copepoda

3. Rotatoria

TRTET = Trichotria tetractis tetractis

KEQUA = Keratella quadrata CEGIB = Cephalodella gibba

ASPER = Asplanchna priodonta (vereinzelt A. girodi)

SYSPC = Synchaeta spec. (oblonga?)

POREM = Polyarthra remata

FILON = Filina longiseta longiseta

XSPC = Species X

SUROT = Summe der Rotatoria

4. Ostracoda

OSJUV = juvenile Ostracoda SUOST = Summe der Ostracoda

5. Sonstige Gruppen

CHIRO = Chironomidae CHAGB = Chaoberus sp.

SUMZB = Summe des Makrozoobenthos

												1000000	- 144.070.02					
	DATUM										POPED					MYA	COS	20000
	130572	0	0	1.5	20	0	0	0	0	10	0	1,500,000			0	70	2	12.2
1 2	130532	0	0	1.4	20	0	0	0.2	0	6	0	21.6	0.2	0	0	14	4.4	13.5
13	130592	0	0	5.2	22	0	-				0	31.2	0.2	0	0	13	1	13.2
14	130592	0	0	0.6	8	0	0	0	0	0	0	8.6	0	0	0	54	0.4	54.4
4 5	130532	0	0	1.4	14	0	0	0	0	22	0	37.4	0.4	0	0			\$1.2
	130592	0				0			0						0.75			51.4
W			0		15.66		355	0.033	0	20.57			0.233					12.83
				***		. Š							•	•			10.000	14.03
1.1	200592	1	0.4	11.4	35	0	11.8	0	9	30		89.6	0	0	0			
	200532	i						0	0							10000	. 12	38
								3 50	- 87	70577.54		146.4		1 5				90
	200532	1					0.700					55.2					8.5	53.4
	200592	1			36		2		0			10000					1	53.6
	200532	1		100		0	97			10		1/1/200				51	10	64.4
1 5	200532	1			25	0	257	7.		// // // // // // // // // // // // //	1 32000		0.5					
86			0.056	20.58	54.45	0.1	5.15	0	0	21.88	0.056	102.9	0.4	0	0	52.53	19.71	63.66
A 1	270592	14	0	4.8	50	1	9.4	C	0	12	0.4	80.6	0.4	0	0	46	8	54.4
1 2	210532	14	0.2	1.4	30	2	0	0	2	2	3	40.5	0	0	0			
	270592	14				5	10	0	0					0	0	215		
	270592	14	. 85															
	270512	14							0									50.4
	270592								0									
				6.255					0							100	- 15 B	
H4			0.032	0.233	31.13	3.322	4.9	ų.	U	29	1.5	30.3	0.132	U	0.022	63.16	16.19	51.1
		2022	A 60.00	12	174		201			0.00	- 1	2000			- 14	0.0		2514
	100532								87			100000		(F)	177			21.5
	100532	28					1266	0				673755			0.73			24
13	100592	28	0	100000		2.9	1		200	2.6	1.2	16.5		0	3	5.4		
11	100593	25	0.2	0.5	45	4		C		2	2	53.8	1.4	0	0	8	8	17.4
4 5	100592	23	0	14	44	0			0	8	2	12	0.5	0.2	0.2	18	10	29
1 5	100532	25	0	10	41	0	0	0	0	8	2	64	4.2	0	0	12	16	32.2
X14			0.1	5.2	30.23	1.455	1	0	0	5.433	2.855	45.75	1.655	0.033	0.033	10.9		22.93
				100000														
1 1	20792	55	0	1.4	24	0	ņ	0	0	6	0	31.4	1.8	0	0	32	22	55.8
	80792								200		- 0		S. SERVE	15		a comme		
	80792	Si					10.5								0			
									0	2					0			
	83732								0						0			
									· ·	16								
	80792	23		10					0	2						20		
Xa			0	3.4	27.66	1.133	0	0	0	5	0	37.2	1.355	0.055	0	25.33	18.33	45.1
	20932			1.5				0				41.6						97.2
	20932			4		2	0	0	0							62		
13	20992	112	0	1.8	25	2	0	0	9			111.8			0	50	25	15.5
1 4	20992	112	2	1.6	12	2	0	0	0		0					54	23	83
	20932						0		0	50	0	62.6	0.6		0	40	42	82.6
	20932								0							50		
M				3.933						35.66		59.5					24.33	
							1.5		1.5			W YARRAY		1.				10000

combining

T	P	BATUM	TAG	INTET	RESUA	CEGES	ASPER	SYSPO	POREN	FILON	1370	SURDT	VULSO	SUCST	CHISO	CHACE	20a13
Å	1	130532	0	0	2	0	20	0	0	0	0	22	0	0	G	0	0
¥	2	130592	0	0	0	0	15	0	0	0	0	15	0	0	9	0	0
Å	1	120532	0	0	0	0	12	0	0	0	0	12	0	0	0	0	C
Å	4	130552	0	0	0	0	6	0	2	0	0	8	0			0	0
Å	5	120592	0	0	0	0	15	0	2	0	0	13	0.2	0.2	0.2	0	0.2
Å	6	130592	0	0	0	2	14	0	6	0	0	22	0	0	0.2	6	0.2
¥	1			0	0.333	0.333	14	0	1.565	0	0	16.33	0.033	0.033	0.056	0	0.055
		200532	î	0	0	0	0	0	4	0	0	4	12			0	1
		200532	1	0	0	0	6.7	0	13.3	0	0	20	6.1	5.7	0	0	0
		200532	1	0	0	0		C	15	0	0	15	0	0	0	0	0
ķ	4	200532	7	C	0	0	9.0	9	4	0	0	4.8	1	1	0	0	0
¥	5	200112	1	0	0	0	6	0	8	0	0	14	1	4	0	0	0
¥	5	200532	7	0	0	0	2.4	0	4	C	0	6.4	2	2	0	0	0
1	1			0	0	0	2.65	0	8.216	0	0	10.85	4.283	4.253	0.155	9	0.155
		270592	14	0	6	0	0	2	4	0	0	6	0	0	: 3	0	0
		270:32	14	0	0	0	2		0	0	0	4	2			0	0
		270532	14	0	0	G	9	5	5	0	0	10	5			0.2	0.2
		270532	14	0	0	0	0	2	C	0	G	2				0.4	9.6
		210:32	14	0	0	ű	0	Û	2	0	0	2	12	12	0	0.2	0.2
		210552	14	0	0	G	2	1	9	0	0	•	2	2		0	0.2
•	1			0	9	0	0.555	2.5	1.533	0	3	5	4.5	4.5	0.065	0.133	0.2
		100572	28	0	0	6	(3)	0	0	0	0	0	- 37			ũ	3
		100532	28	0	G	0	0	0	177	0	0	0	0	0		0	0
		100892	25	0	C	9		17	3,50	0	Û		125 7007			9	3
		100692	23	G	0	0	9	0	0	C	5	2	0.4			0	0
		100532	25	0	0	G	0		0	9	0	4 5	0			0	0
		100593	23	0	0	0			C	C	0	G	û	Ð		0	
K.	(0	0	0	C	C	0	0	0	0	0.1	0.1	0	0	0
1		80792	55	C	0	0	1 7	ė	0	0	0		0		9	0.4	0.4
1		80792	56	0	0	0	0	0	0	0	0	0	2			0.2	
¥		80792	56	0	0	0	0	6	0	0	0	0	0			0.6	0.6
¥		86792	55	0	0	0	0	0	0	0	0	0	0			0.5	0.5
Å		80792	55	0	0	0	0	- 55	0	0	0	0	0			0.2	0.2
		80792	55	0	0	0	-	1000	0	0	0	2	0			0.2	0.2
K	1			0	0	0	0	1.333	0	0	0	1.333	0.333	0.333	0	0.355	0.366
Å		20992								0			0			0	0
٨		20992								0	0		0				0.5
٨		20992		0						0	0			0			
٨		20032		0	-					0	0		0	1.00		0	
¥		20335								0	0		6			0.2	0.2
A		20932	112	0						0	0	TOTAL TOTAL	0		La 2000	0	
K				0	97	0	0	0	15.33	0	0	173.3	1	1	0.233	0.165	0.5

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	DATUM								ALAF	CHYSP	POPED	SUCLD	EliAnt	CYSTR	EUSER	NAU	COP	SUCOP
	130532	0	. 3		5.6	0	100	0	0	4.2	ſ	12.4	0.6	0	9	75.2	1.2	11
39.73	130532	0			3.6	0	10.7		0	2.8	0		0	0	0	10.5	0.8	11.4
	130592	0	0	1.8	10	0	G.4	0	٥	18	0	30.2	0.4	0	0	154	6.5	171.2
	130532	0	0	4	14	0	0.4	0	0	10	0	28.4	0.4	0	0	25	2.2	88.6
8 5	130592	0	0	1.6	10	0	2	0	0	14	0	27.6	0	0	0	64	0.4	64.4
	130532	0	0	1.2	6.2	G	0.4	0	0	8	0	15.8	0.6	0	0	74	3.8	13.4
MA			0	1.966	8.233	0	0.533	0	0	9.5	0	20.23	0.333	0	0	83.95	2.523	91.53
					1000													
1.5.5	200592	1	0		64	0	1.5	0	9	1 22	2		0.6	0	0	25	10	18.5
	200532	1	0.4		22	0	177	0	0		0	21.2	0.2	0	0	44	8	52.2
	200592	1	C		14	0		0	G		G	85.6	0.6	0	0.4	50	20	11
	200592	1	0		22	0	177	0	0	A 2073	0	33.2	0.2	0	0	34	15	50.2
	200532	1	C	12.8	32	0	1000	0	0	16	0	56	0.4	0	9	25	4	30.4
8 \$	200592	1	0.2	5.2	42	0		0	0	A	0.4	47.8	!	0	0	34	8	+3
MA			0.1	4.933	32.55	0	2.1	0	C	17.65	0.4	56.8	0.5	0	0.056	35	11	41.56
	270532	11	0	5.7	60	0	11.2	0	0	13.3	0	90.2	3.1	0	0	43.3	20	67
8 2	270592	11	0	1.4	52	2	2	0	0	6	0	63.4	0	0	0	22	25	49
8 3	270592	14	0	6.7	49	0	15.1	0	0	\$3.3	0	145.1	0.4	0	0	110	30	140.4
3 4	270592	14	0	2	25	0	2.4	0	0	14	0.4	44.8	4.2	0	0	40	22	65.2
8 5	270532	14	0	0	25.1	0	5.7	0	1.3	39	1.3	69	0.4	0	0.4	13.3	25.7	100.8
8 6	270532	14	1	0	44	0	0	0	0	14	2	61	2.4	0	9	30	12	41.4
44			0.155	3.633	41.45	0.333	6.056	0	0.55	25.76	0.95	19.91	1.85	0	0.055	53.1	22.78	17.8
8 1	100592	23	0.2	2.2	3	0	2.5	0	0	14	0	27	0	0	0	58	12	11
3 2	100532	23	0	0	3.4	0	0.3	0	0	4	0	8.2	3.8	0	C	56	15	15.8
8 3	100532	23	0.2	0.8	2.9	0	1.8	G	G	10	0	15.6	2.4	0	0.2	54	29	15.5
8 4	100592	23	0.2	C	6	0.2	5.2	0	0	15	0	27.6	4.6	0	0	83	18	102.5
8 5	100592	23	0	3.4	6	C	0	0	0	6	0	15.4	0.8	0	0	68	15	84.8
8 6	100592	23	4.8	0.8	8	0	0.1	0	0	0	0	14	1.4	0	0	52	14	67.4
N'4			0.9	1.2	5.1	0.033	1.5	0	0	8.333	0	17.96	2.166	0	0.033	61.33	15	79.53
8 1	80792		0		4	2	0	0	0	2	0	8.4	1.8	0	0	14	20	95.8
8 2	86192	50	0.4	0	13	0	0	0	0	2	0	20.4		0	0	90	25	119
8 3	80792	55	0	. 52	13	10	0.2	0	0	4	0	32.2		0	0	76	16	95.2
8 4	80792	55	0.4	0	25	0	3	0	0	2	0	23.4	2.2	0	0	78	20	100.2
8 5	80792	55	0	0	6	2	2	0	C	2	0	12	1.5	0	0	64	14	79.6
3 6	80732	55	0.4	6	li.	1	0	9	0	2	0	58.4	5	0	0	102	35	143
A.A.			0.2	1.065	19.65	3	0.365	0	0	2.333	G	25.63	2.633	0	0	80.65	2?	105.3
8 1	20992	117	0.2	2	14	2	1	0	0	15	٥	35.2	0	0	0	98	20	118
8 2	20992				14	0	2	0	0		0	21.8			0			200.4
8 3	20992					0	ò	0	1		0	25.4			0			111
1 1	20992				6	0	3.6	0	0		0	26		0	0			223.5
9 5	20932				5.1	0	6.1	0	0		0	80.1			0		113.3	
8 6	20932				18	0	0	0	0		0	33.2		0	0	142		174.6
MA	.,,,,		0.733		11.11			0	27	21.45	17		0.733		. 7		45.55	
			4.123	6.1	11,11	4.333	2.210				•	21.33		4.4.1		131.3	41.33	111.0

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Name 20.00

and delication

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FI

T P	DATUM	TAG	TRIET	REQUA	CEGIS	ASPER	SYSPS	POREM	FILON	ISPC	SUROT	VULZO	SUGST	CHIRO	ECHADE	SUNZE
8 1	130592	C	0	0	0	4.2	0	0.8	0.6	0		0	0		0	0
8 2	130592	0	0	0	0	19.4	0	1	0	0	20.4	0	Û	0		0
8 3	130592	0	C	0	0	28	0	8	0	0	35	0.6	0.6	0	0	ũ
	130532	0	0	0	0	30	0	0	0	0	30	2	2	0	C	0
	130592	0	0	0	2	6	0	0	0	0	8	0	0	0	0	0
8 6	111132	0	0	0	0	4	0	0	0	0	4	0	0	0	0	0
X1			0	0	0.333	15.25	0	1.633	0.1	0	17.33	0.433	0.433	0	0	0
	200592	7	0	0	0	2	0	0	ũ	0	2	4	4	0.4	0	0.4
	200532	1	0	0	0	0	0	2	0	0	2	2	2	0	0.2	0.2
	200532	1	0	0	ů	4	0	0	0	0	4	14				2
	200592	1	0	0	0	8	0	0	0	0	8	14			0	0.4
	200592	1	0	0	0	0	0	0	0	0	0	2	2	0	0	0
	200592	1	0	0	C	G	C	0	0	0	0	0	0		0	0
W			0	G	0	2.333	0	0.333	C	0	2.666	6	6	0.456	0.033	0.5
	270592	14	0	0	0	0	5.7	0	0	0	6.7	3.3	3.3	0	0	0
	270592	14	0	Ú	0	0	6	0	0	0	6	1			0	0
	270532	14	0	0	0	0	45	0	0	0	-	20	20		3.3	3.3
	270592	14	0	0	0	0	34	0	0	0		6	6		0	0.2
	270532	14	0	1.1	0	0	25.7	0	0	0		40	43		0	0
	270592	14	0	0	0	0	12	0	0	0	12	10	10		0	0.2
KI			0	0.55	0	0	20.9	0	0	0	21.45	13.88	13.88	0.065	0.55	0.516
	100632	25		0	0	0	16	C	0	0	20				0	0
	100592	28	0	0	0	0	40	2	0	2	44					1
	100692	28		0		0	34	0	0	2					0.2	
	100592	23		0	2	0	34	0	0	0	44				0	0.5
	100632	28	2	0	0	0	33	0	0	4		0		1.5	-	0.2
	100692	28	1	0	0	0	32	0	0	0		0	0		0	0
W			2.5	0	0.333	0	32.33	0.333	0	1.333	31	1.333	1.333	0.265	0.166	0.433
8 1	80792	:5	0	U	0	0	0	2	0	0	2	0	0	1.5	0.6	0.6
8 2	80792	55	0	2	0	0	0	0	0	0		0		22.5	0.4	0.4
8 3	80792	56	0	0	0	0	3	2	0	2		2			0.4	0.4
8 4	80792	56	0	0	0	0	0	2	0	0		0	0		1000	1.2
8 5	80792	56	0	2	0	0	2	•	0	0		0	. 5	- 27	0.8	0.8
	80792	56			0			0	0	0.00	2	4		0		
W			0	0.655	0	0	0.111	1.655	0	0.533	1.113	1	1	0	0.5	0.6
	20992				0	0				0			0			
8 2	20992				0	0										
8 3				0	0			88		0						
14	20992			0							95					
8 5	20992						0			950	70					
	20992	112					0									0.8
MA			1.665	0.333	0	0	0	94.55	0	2.116	95.66	1.883	3.883	0.4	0.333	0.133

SHARK SHARK

T	POATUM	TAG	DANAS	DALOR	VULAD	SCHUC	SIVET	BCLON	ALAF	CHYSP	POPES	SUCLO	EUVUL	CYSTR	EUSER	MAU	COP	SUCOP
C	130592	0	2	4.6	42	0				14	0	62.8				75		18.2
C	130592	0			16	0	0		0	2	0	18.6	0	0	0	90		92
	130592				14	0		0		4	Ű	19.4	0.6	0	0	13	4	82.5
	130592				8.4	0		0	0	2.2	0	11.2	0.4	C	0	40	1.5	43
	130592		0.73		9	0	0	G	0	5	0	14.4	0	0	0	50	1.2	51.2
C	130592	0	10.7	7.	4.5	0		0.70	33.70			10.8	0.2	0	0	53	1.4	53.6
MA			0	1.256	15.55	0	0.033	0.333	0	5.565	0	22.85	0.233	0	0	65.33	2.033	67.6
	200592	1	100			0	0.2	0	0		0	55.6	0.2			45	5	54.2
	200592	1	100		200	35	0		0		10.70	36	0	0.50		1717		63
	200592	1	100	40.0			11.2	107		66		194.2		0		58		83.4
43000	200592	1	0.00	2000			2.4			12		31.8		0		58		
	200592		- 34		65.7	(57)	8.1	17	0	43.3				0.2		50		67.5
	200532	i	0		32				0			45.6	0.6	0	-	58		65.5
MA			0	6.35	45.78	0	1.933	0	0	24.21	0.033	81.36	0.633	0.033	0	54.66	14.45	53.78
	270592				3.3	0			0			56.6	1.3			63.3	25.7	3.3
	270592								0			22.6		A		14	20	
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MM			0.355	4.515	35.43	0	0.55	0	0	16.78	0.55	57.55	1.083	0	0	57.31	25.23	1.033
	100532			0.8		0	- 2		0	- 3		1.8						108.5
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114			0.033	6.133	3.15	0	1.7	0	0	1.565	0	18.68	2.366	0	0.033	106.4	28.55	137.4
	80792	55	0	0.6	6	C			0	10	0	16.8	2			56	20	85.4
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MX			0	2.455	25.13	1.333	0.033	0	0	14.33	0	44.5	3.7	1.5	0.5	43.33	18	67.13
	20932				4.5	0.4	0	0		3.3		11.1						247.4
	29992				6.7	0	0.4	0		3.3		- 11						238.5
	20992				13.3				0			140.7				343.3		398.4
	20992				55.7	0			0			71.1				270		312.6
	20992				33.3				0									301
C		112		20.7					0			93.4						253.9
MA			0	6.25	28.55	2.233	5.256	0	0	20.53	0	62.83	1.516	0.356	0.033	271.1	29.45	302.4

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	1 P	DATUM	TAG	TRIET	KEQUA	CESES	ASPER	SYSPO	POREN	FILON	XSPC	SUROT	VULSO	SUOST	CHIRO	CHAOS	SUMZ3
	1	130592	0	0	0	0	33	0	0	0			2	2			0
1	C 2	130592	0	0	0	0	25	0	4	0	0	30	0	0	0	0	0
1	: 1	130592	0	0	0	0	16	0	6	0	0	22	2	2	0	0	
-	: 4	130592	0	0	0	0	10	0	0	0	0	10				0	
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		130592	0	0	0	0	10		0	0		10	9	0		/ // //	0.2
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		270592	14	0	0	0		152.3	0		1 3	155.5	23.3	23.3		0	-
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		270592	14	0	0	0	2	93	0	0	0	100	10	10	0	G	0
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19	11/12														2.2		
		103592	23	8	2	0	0	22	13	0	2	52	0	0	175.00.00	1	1.6
		100532	23	0	6	0	0	22	23	0	0	43	0				0.8
		100632	23	0	2	0	0	13	34	0	4	58	2				0.5
		100532	23	0	4	0	0	20	30	0	0	54	2	2		0.4	0.4
		100532	23	0	6.1	0	0	12	10	0	3.3	30	6.7	6.7	0	0.8	0.3
		109692	23	5	4	0	0	15	22	0	0	41	0	0	0	0.2	0.2
,	11			1.565	4.116	9	0	13	22.33	0	1.55	47.56	1.783	1.733	0.165	0.565	0.733
(: 1	80792	56	0	0	0	0	0	26	0	0	25	4	4	0	0.2	0.2
(: 2	80793	56	0	2	0	0	0	42	0	0	44	0	0	0	0.8	
(: 1	80732	55	0	0	0	0	0	13	0	0	18	2	2	0	0.2	
(: 4	80792	55	0	0	0	0	2	32	0	0	34	0	0		0.4	
(: 5	80792	56	2	0	0	0	0	13	0	2	22	0	0	-		0.5
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(1	20932	112	0	203.3	0	0	10	236.7	0	0	500	3.3	3.3	0	0.2	0.2
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	n				235.8				337.2				6.65				
	77.5					•											

Maria sures.

1. Oligochaeta:

TUBI = Tubificidae NAID = Naididae

2. Hirudinaea:

EROC = Erpobdella octoculata
HEST = Helobdella stagnalis

3. <u>Gastropoda:</u>

RAPE = Radix peregra GYAL = Gyraulus albus

4. Bivalvia:

SPSP = Sphaerium sp. PISP = Pisidium sp.

5. Crustacea:

OSTRA = Ostracoda

6. Ephemeroptera:

CLDI = Cloeon dipterum

7. Diptera:

workers -

CHAOB = Chaoberinae

Chironomidae:

TANY = Tanypodinae CHIRO = Chironominae ORTHO = Orthocladiinae

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LEHRSTUHL FÜR BIOLOGIE V Ökologie, Ökotoxikologie, Ökochenie der Rheinisch-Westfälischen Technischen Hochschule

RWTH Aachen, 52056 Aachen

Declaration

Therewith we declare, that we have performed the statistical evaluation of the phytoplankton-, zooplankton and benthos data from the microcosm experiment conducted in 1992 by the Institute of Ecobiology, Bayer AG, to the best of our knowledge and beliefe as well as according to the common scientific standard. The data to evaluate was been collected by aqua terra, Institut für angewandte Ökologie e.V., Köln.

Aachen, 17.06.93

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Udo Hommen

- microcosm experiment 1992, Bayer AG, Leverkusen-Monheim

The data has been sent to us as common QuattroPro, Lotus or ASCII-files on floppy discs, collected by aqua terra, Institut für angewandte Ökologie e.V., Köln.

For the statistical evaluation we used the PC-program CA (Community Analysis, Hommen et al. 1993).

The results of the program had been verified by test data sets (e.g. Smith 1986, Mühlenberg 1976) and by comparison with another, independent statistical programs (Pelzer, unpubl.).

The following calculations have been conducted:

1. Calculation of means

Arithmetic means were calculated from the up to 6 samples per pond for the most abundant species or taxa. These means were used for the plots. The differences were tested for significance using t-test, Wilcoxon-Mann-Whitney-test, ANOVA or Kruskall-Wallis-test (depending of the type of distribution).

2. Number of species, diversity and eveness

For the zooplankton we had to lump some groups which had been separately counted but could not be assigned to one certain species:

a) Zooplankton

1

Daphnia magna + D. long. + D. juvenile = Daphnia spec. adult Copepods + copepodits + nauplii = total Copepods juvenile Ostracods + adult Ostracods = total Ostracods

Therefore, the following 19 taxa have been considered (see list of abbreviations):

DASPEC SCMUC SIVET BOLON ALAF CHYSP POPED SUCOP TRTET KEQUA CEGIB ASPER SYSPC POREM FILON XSPC SUOST CHIRO CHAOB

For the phytoplankton, all of the 53 counted units by aqua terra could been used as seperate species:

COEKU PSAAR ACNOR AMPPS AULIT CALBA CYCME CYMVE DIHIE DITEN DIVUL FRACR GOMSP NACUS NASUB NASPC NICAP NIFON NISUA STANC SYNAC DIUND EUSPC PHOSC PHPLE PHPYR TRSPC CRERO CRMAR CHNOR RHGLA COLMI COCFO DICPU LAGGE OOSPC PLALA SCARC SCARM SCART SCELL SCOBL SCSEM TECAU TEKOM CHLUN CSEHR CSLUN CSPRI CSPRO COLAE COMEN CJUND

The similar was done for the counted benthos taxa (14), they all were used for calculation of the diversity indices:
BI NAID EROC HEST RAPE GYAL SPSP PISP OSTRA CLDI CHAOB TANY

BI NAID EROC HEST RAPE GYAL SPSP PISP OSTRA CLDI CHAOB TANT

To determine the species number, species or taxa have been taken that occurred at least in 1 individual and 1 sample per pond.

As a measure of diversity the Shannon-Weaver index was used (e.g. Boyle et al. 1990).

$$H_S = - \Sigma p_i * ln(p_i)$$

with \mathbf{p}_i : relative population density of species i

The eveness as calculated by (e.g. Boyle et al. 1990):

$$E = H / H_{max} = H_S / ln(n)$$

with n : number of existing species

3. Similarities

To calculate similarities of communities we used the same data sets as described above (2.).

The Stander's index was calculated according the following formula (e.g. Boyle et al. 1990):

$$s = \Sigma(p_{ik} * p_{jk}) / (\Sigma p_{ik}^2 * \Sigma p_{jk}^2)^{0.5}$$

with:

i, j : samples to compare

 p_{ik}, p_{jk} : relative population density of species k in sample i and j

The randomized permutation procedure by Smith (1986) is described in detail in Engels & Ratte (1992) (see enclosure).

References

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List of	the abbreviations used by	aqua SCOBL	Scenedesmus oblique
terra		SCSEM	Scenedesmus sempervirens
		TECAU	Tetraedron caudatum
1. Algae (19	021	TSKOM	Tetrastrum komarekii
. Algee (15		CHLUN	Chlorophyceen, not specified
Cyanophyces	162		
COECU	Coelosphærium kuetzingianum	Conjugat	ophycese:
PSAAR	Pseudoanabaena articulata	CSEHR	Closterium ehrenbergii
		CSLUN	Closterium Iunula
Diatomese:		CSPRI	Closterium pritchardianum
ACNOR	Actinocyclus normanii	CSPRO	Closterium pronum
AMPSP	Amphora spec.	COLAE	Cosmarium laeve
AULIT	Aulecoseira italica	COMEN	Cosmarium meneghenii
CALBA	Caloneis bacillum	PSSSP	Pseudostaurastrum spec.
CYCME	Cyclotella menegheniana	CJUND	Conjugat, not specified
CYMVE	Cymbella veritricosa		
DIELO	Diatoma elongatum	CYANO	Sum of Cyanophyceae
	The second secon	DIATO	Sum of Distomese
DIHIE	Diatoma hiemale	EUGLE	Sum of Euglenophycese
DITEN	Diatoma tenuis	CRYPT	Sum of Cryptophycese
DIVUL	Diatoma vulgaris	CHLOR	Sum of Chlorophycese
FRACR	Fragilaria crotonensis	CONJU	Sum of Conjugatophycese
GOMAC	Gomphonema acuminatus		
NACUS	Navicula cuspidata		
NAPER	Navicula peregrina	2. Zoopi	ankton (1991)
NASUB	Navicula subrhynchocephala	A1.77.76	
NASPC	Navicula spec	Cladocer	•
NICAP	Nitzschia capitellata	-	
NIFON	Nitzschia fonticols	DAMAG	Daphnia magna
NILIN	Nitschia linearis	DALON	Daphnia longispina
NISUA	Nitzschia subacicularis	DAJUV	juvenile Daphnia (mostly D. longispina)
PINME	Pinnularia mesolepta	SCMUC	Scapholeberis mucronata
STANC	Stauroneis anceps	SIVET	
SYNAC	Synedra acus	BOLON	Simocephalus vetulus
DIUND	Diatomeen, undeterminiert		Bosmina longirostris Acroperus harpae
		ACHAR	
Euglenophyo	:000:	CHYSP	Chydorus sphaericus
EUSPC	Euglena spec.	POPED	Polyphemus pediculus
PHOSC	Phacus oscillans	SUCLD	Summe der Cladocera
PHPLE	Phacus pleuronectes		
PHPYR	Phacus pyrum	Copepo	<u>1.</u>
TRSPC	Trachelomonas spec		
		EUVUL	Eudiaptomus vulgaris
Cryptophyce	rae:	CYSTR	Cyclops strenuus
CRERO	Cryptomonas erosa/ovata	NAU	Nauplien
CRMAR	Cryptomonas Marssonii	COP	Copepodite
CHNOR	Chroomonas nordstedti	SUCOP	Summe der Copepoda
RHOLA	Rhodomonas lacustris		
Miloca	Taradamente lacostrie	Rotatori	
Chlorophyce			
COLMI	Coelastrum microporum	BRCAL	Brachionus calciflorus
COCFO	Coenococcus fortii	KEQUA	Keratella quadrata
		CEGIB	Cephalodella gibba
DICPU	Dictyosphaerium pulchellum	ASPER	Asplanchna priodonta (vereinzelt A. giroc
LAGGE	Lagerheimia genevensis	SYSPC	Synchaeta spec. (oblonga?)
KIRSU	Kirchneriella subcapitata	POREM	Polyarthra remata
OOSPC	Oocystis spec.	FILON	Filina longiseta longiseta
PLALA	Planctonema lauterbornii	XSPC	Species X
SCARC	Scenedesmus arcuatus	SUROT	Sum of Rotatona
SCARM	Scenedesmus armatus	301101	
SCART	Scenedesmus arthodesmiformis		4
SCELL	Scenedesmus ellipticus	Ostraco	<u>0.</u>

OSJUV juvenil Ostracoda SUOST Sum of Ostracoda

Other Taxa

CHIRO Chironomidae

CHAOS Chaoborus sp.

SUMZB Sum Makrozoobenthos

3. Benthos (1991)

Oligochaeta

TUBI Tubificidae

NAID Naididae

HIRUDINEA

EROC Erpobdella octoculata

HEST Helobdella stagnalis

BIVALVIA

SPSP Spheerium sp.

PISP Pisidium sp.

CRUSTACEA

OSTRA Ostracoda

EPHEMEROPTERA

CLSI Closon simile

DIPTERA

CERAT Ceratopogonidae

CHAOB Chaoboridae

CHIRONOMIDAE:

TANY Tanypodinae

CHIRO Chironominae

ORTHO Orthocladiinae

: 01.10.92

GLP Final Report

ACCOMPANYING ANALYSIS FOR POND STUDY

BAYER AG		Date	: O5.Feb.1993
Central Analysis De	epartment	Study number	: G 92/0061/01 LEV
51368 Leverkusen		Study director	: Dr. Jaeger
Germany		Deputy	: Dr. Theimer
Test substance: Poly	ymeric MDI (Desmodu	nr 44 V 20)	
III representative: D	Dr. Klebert, Bayer AG	, Dormagen	Commission No
Chemical name :			
Empirical formula		Molar mass	: g/mole
CAS No.	:	Batch/lot No.	: 2014
Sample No./year:	432732/1992	Sample date	: 01.04.92
Production plant:	PU-P/UER	Production date	: 01.04.92

Start of study : 13.05.92 End of study : 13.01.93

Product No .:

1. Objective of the study

Study 101-EU-ENV organized by the International Isocyanate Institute (III) involves a simulated transport accident in which polymeric 4,4'-diphenylmethane diisocyanate, also known as 4,4'-methylenediphenyldiisocyanate (MDI), enters an aquatic ecosytem. This aquatic ecosystem was simulated using three artificial ponds. A detailed description of the study can be found in the study plan for study No. E 413 0629-5 (managed by Dr. Heimbach, PF-F/UF-OE). The test substance was added to the three ponds as follows:

Stable until

Pond A: Control

Pond B: 1 g MDI/l pond water Pond C: 10 g MDI/l pond water

410 012 01

Frequency: Single dose.

Accompanying analysis for the pond study was carried out by the Central Analysis Department, Leverkusen (Dr. Jaeger and Dr. Fus) under study No. G 92/0061/01 LEV. It encompassed analysis of the sample matrices water, fish and sediment for monomeric MDI (4,4'-diphenylmethane diisocyanate) and MDA (4,4'-diphenylmethanediamine).

ACCOMPANYING ANALYSIS FOR POND STUDY

Date of sampling	Type of sample
Day -1 May 12, 1992	Sediment
Day 0 May 13, 1992	Water
Day 1 May 14, 1992	Water
Day 7 May 20, 1992	Water, sediment
Day 14 May 27, 1992	Water, sediment
Day 28 June 10, 1992	Water, sediment
Day 56 July 8, 1992	Water, sediment
Day 112 September 2, 1992	Water, sediment, fish

The sediment samples were mostly mixed samples obtained from six individual samples. The sampling locations are described exactly in study E 413 0629-5. The following target limits of detection for MDA and MDI were established in the project proposal for the International Isocyanate Institute:

Water: 0.1 mg/l
Sediment: 1 mg/kg
Fish: 1 mg/kg.

2. Characterization of the test substance

The material accountability of the test substance polymeric MDI (batch/lot No. 2014, sample No. 432732/1992) was analyzed under study No. G 92/0061/00 LEV (study director Dr. Fus)

3. Brief description of the analytical methods

3.1 Extraction and enrichment of MDA and MDI from aqueous solutions (analytical method 2011-0326201-92D)

In the aqueous sample, MDI was derivatized with dibutylamine to give 4,4'-diphenylmethane-N,N'-dibutylurea (HPLC determination) or with N-(4-nitrobenzyl)propylamine (TLC determination) to give the corresponding urea. 4,4'-Diphenylmethane diamine and the urea derivative were then extracted with toluene and the extract was concentrated using a rotary vacuum evaporator. The concentrated sample solution derivatized with N-(4-nitrobenzyl)propylamine (nitroreagent) could be analyzed directly by TLC (thin-layer chromatography). If MDI in the water sample was derivatized with dibutylamine, it was quantified by HPLC (high-performance liquid chromatography). The result could not be confirmed

ACCOMPANYING ANALYSIS FOR POND STUDY

by MDI recovery before the organic toluene phase since MDI precipitates immediately as urea in water. Under these conditions, the mean recovery rate for MDI was 90 % with TLC; the mean recovery rate for MDA was also 90 %.

3.2 Extraction and enrichment of MDA and MDI from trout (analytical methods 2011-0322401-92D and 2011-0322301-92D)

The frozen, sacrificed trout were homogenized. Any MDI which existed was derivatized with dibutylamine to 4,4'-diphenylmethane-N,N'-dibutylurea and extracted with toluene. The toluene extract was concentrated with methanol and analyzed by HPLC. To determine MDA, the homogenized fish was extracted with diethylether, and the concentrated extract solution was analyzed by HFLC. When analytical methods 2011-0322401-92 D and 2011-0322301-92D were established, MDA was added to the homogenized fish and MDI to the diethylether extract. The mean recovery rates were 69 % for MDA and 84 % for MDI.

3.3 Extraction and enrichment of MDA and MDI from pond sediment (analytical methods 2011-0322101-92D and 2011-0322201-92D)

The pond sediment was homogenized with sodium sulphate and any MDI in the sediment was derivatized with dibutylamine to 4,4'-diphenylmethane-N,N'-dibutylurea. The urea was extracted with toluene. This extract was then concentrated and analyzed by HPLC. Determination of MDA was carried out analogously using diethylether for the extraction step. When the analytical methods were established, recovery rates were determined by adding MDA to the sediment and MDI to the toluene extract. The mean recovery rates were 56 % for MDA and 82 % for MDI.

3.4 HPLC determination of the MDA content in the extracts obtained in sections 3.1 - 3.3 (analytical method K 2011-0322501-92D)

Subject: MDA content in extracts from samples of fish, sediment and water

Method No.: K 2011-0322501-92D

Description: HPLC method

Isocratic

Eluent: 300 ml acetonitrile, 700 ml distilled water, 2 ml o-phosphoric

acid

Column: Cyclobond I (b-cyclodextrin, Astec Cat. No. 41010), length 250 mm, internal diameter 4.6 mm, flow rate about 1 ml/min, UV detection at 220 nm, evaluation against an external standard.

ACCOMPANYING ANALYSIS FC POND STUDY

3.5 HPLC determination of MDI content in the extracts obtained in sections 3.1 - 3.3 (analytical method K 2011-0322601-92D)

Subject: MDI content in the form of the derivative 4,4'-diphenyl-

methane-N,N'-dibutylurea

Method No.: K 2011-0322601-92D

Description: HPLC method

Gradient elution

Eluent A: 300 ml acetonitrile, 700 ml distilled water, 2 ml

o-phosphoric acid

Eluent B: 1000 ml acetonitrile, 2 ml o-phosphoric acid

Gradient:

Min	A %	В %	ml/min
t = 0	100	0	1
t = 4.0	100	0	1
t = 4.1	100	0	1.5
t = 9.0	40	60	1.5
t = 20.0	40	60	1.5
t = 25.0	100	0	1.0

Column: RP8 commercial column (Merck Cat. No. 50341), length 250 mm, internal diamter 4.6 mm, timer-controlled UV detection at 220 - 250 nm, evaluation against an external standard.

3.6 Details of the linearity and precision of the HPLC determinations of MDI and MDA

The linearity of the determination procedure for MDI and MDA using the above analytical methods (sections 3.4 - 3.5) was verified over a range of 0.5 - 10 mg/l using six different concentrations of standard solutions. When the enriched sample extracts were quantified, a calibration point was set at 10 mg/l. The evaluation follows the procedure of an external standard. The precision of the method was established with six independent determinations of standard solutions containing 2 mg/l.

ACCOMPANYING ANALYSIS FOR POND STUDY

MDA	MDI derivative	
1.99 mg/l	2.01 mg/l	Arithmetic mean
0.10 mg/l	0.04 mg/l	Standard deviation
0.36 mg/l	0.15 mg/l	Range
0.11 mg/l	0.04 mg/l	Uncertainty of measurement
1.99 ± 0.11 mg/l	$2.01 \pm 0.04 \text{ mg/l}$	Confidence interval

The limits of detection were 0.5 mg/l for both MDA and MDI based on the standard solutions.

3.7 Determination of MDI and MDA content in aqueous solutions (see section 3.1) by thin-layer chromatography (analytical method 2011-0326301-92D)

The content of MDI and MDA in the extracts of the water samples (section 3.1) was also determined by thin-layer chromatography to confirm and supplement the HPLC determinations. The principle is the reaction of MDI in the test solution with N-(4-nitrobenzyl)propylamine (nitroreagent) to form the respective urea derivative. (The MDA remained underivatized.) This reaction prevents the isocyanate from reacting further with the water and allows a visualization of the spots after thin-layer chromatography. To achieve this, the nitro group of the nitroreagent ureas is reduced, then diazotized together with MDA and coupled to the corresponding azo dyes. Evaluation is then performed visually using an external standard.

MDA and the MDI derivative were determined on one chromatogram on the basis of their different R_F values and different colours on the plate.

Test: Content of MDA and MDI in extracts from water samples

Method No.: 2011-03263201-92D
Separation chamber: Flat-bottom chamber
Layer: Silica gel 60 F 254

Layer thickness: 0.25 mm

Solvent: Acetone/toluene 4 ml/6 ml Application volume: $10 \mu l$ of each solution

Separation path: About 7 cm
Development time: About 30 min

ACCOMPANYING ANALYSIS FOR POND STUDY

4. Results

4.1 Test: Content of 4.4'-diplyenylmethane diamine in water samples

Sample preparation

method No.: 2011-0326201-92D

TLC method No.: 2011-0326301-92D

Laboratory manager: Dr. Fus

HPLC method No.: K 2011-0322501-92D

Laboratory manager: Dr. Jaeger

		HP	LC	TLO	
Day	Date	Pond B mg/l	Pond C mg/l	Pond B mg/l	Pond C mg/l
0	13.05.92	n.d. < 0.0125	n.d. < 0.0125	n.d. < 0.0125	n.d. < 0.0125
1	14.05.92	n.d. < 0.125	n.d. < 0.0125	n.d. < 0.0125	n.d. < 0.0125
7	20.05.92	n.d. < 0.0125	n.d. < 0.0125	n.d. < 0.0125	n.d. < 0.0125
14	27.05.92	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01
28	10.06.92	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01
56	08.07.92	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01
112	02.09.92	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01	n.d. < 0.01

n.d. = not detectable, recovery rate (see section 3.1) not taken into account

The limits of detection given here vary depending on the volume of the concentrated sample. On days 0, 1 and 7 200 ml of water were used; on the other days the sample volume was 250 ml.

ACCOMPANYING ANALYSIS FOR POND STUDY

4.2 Test: Content of 4,4'-diphenylmethane-N,N'-dibutylurea in water

samples

Sample preparation

method No.:

2011-0326201-92D

TLC method No.:

2011-0326301-92D

Laboratory manager: Dr. Fus

HPLC method No.: K 2011-0322601-92D

Laboratory manager: Dr. Jaeger

		HPLO		TLC	
Day	Date	Pond B mg/l	Pond C mg/l	Pond B mg/l	Pond C mg/l
0	13.05.92	n.d. < 0.0125	n.d. < 0.0125	n.d. < 0.025	n.d. < 0.025
1	14.05.92	n.d. < 0.125	n.d. < 0.0125	n.d. < 0.025	n.d. < 0.025
7	20.05.92	n.d. < 0.0125	0.0178	n.d. < 0.025	n.d. < 0.025
14	27.05.92	n.d. < 0.01	0.0533	n.d. < 0.02	n.d. < 0.02
28	10.06.92	n.d. < 0.01	n.d. < 0.01	n.d. < 0.02	n.d. < 0.02
56	08.07.92	n.d. < 0.01	n.d. < 0.01	n.d. < 0.02	n.d. < 0.02
112	02.09.92	n.d. < 0.01	n.d. < 0.01	n.d. < 0.02	n.d. < 0.02

n.d. = not detectable, recovery rate (see section 3.1) not taken into account

The limits of detection g: here vary depending on the volume of the concentrated sample. On days 0, 1 and 7 200 ml of water were used; on the other days the sample volume was 250 ml.

ACCOMPANYING ANALYSIS FOR POND STUDY

4.3 Test: Content of 4.4'-diphenylmethane diamine in pond sediment

Sample preparation

method No.:

2011-0322201-92D

HPLC method No.: K 2011-0322501-92D

Laboratory manager: Dr. Jaeger

Day	Date	Pond mg/l		Pond mg/k	
-1	12.05.92	I	n.d. < 0.58	I	n.d. < 0.5
		П	n.d. < 0.58	II	n.d. < 0.5
7	20.05.92	I	12.88	I	8.1
		II	n.d. < 0.58	П	33.9
14	27.05.92	I*	n.d. < 0.58	I**	n.d. < 0.5
		II*	n.d. < 0.58	П**	n.d. < 0.5
28	10.06.92	I	n.d. < 0.58	I	1.6
		II	n.d. < 0.58	п	n.d. < 0.5
56	08.07.92	I	n.d. < 0.58	I	n.d. < 0.5
		II	n.d. < 0.58	П	2.1
112	02.09.92	I	n.d. < 0.58	I	n.d. < 0.5
		П	n.d. < 0.58	II	n.d. < 0.5

I, II: Sample identification, all contents determined by HPLC

* : The sediment samples from positions 1-6 in pond B were supplied separately and combined to form a mixed sample

I**: Sediment sample from position 1 in pond C II**: Sediment sample from position 3 in pond C

n.d.: Not detectable, recovery rates (see section 3.3) not taken into account

ACCOMPANYING ANALYSIS FOR POND STUDY

4.4 Test: Content of 4,4'-diphenylmethane-N,N'dibutyl-urea in pond

sediment

Sample preparation

method No .:

2011-0322101-92D

HPLC method No.: K 2011-0322601-92D

Laboratory manager: Dr Jaeger

Day	Date	Pon mg/		Pone mg/	
-1	12.05.92	I II	n.d. < 0.58 n.d. < 0.58	I	n.d. < 0.5 n.d. < 0.5
7	20.05.92	I II	25.2 3.2	I II	20852 17968
14*	27.05.9?	I II	0.9 11.2	1 2 3 4 5 6	33931 28529 19883 10034 41069 951
28	10.06.92	I	2.6 2.7	I II	7860 7878
56	08.07.92	I II	3.2 1.3	I	3161 5089
112	02.09.92	I II	n.d. < 0.5 2.1	I	1.3 1.8

n.d.: Not detectable, recovery rates (see section 3.3) not taken into account

I, II: Sample identification, all contents determined by HPLC

: On day 14 six individual samples were analyzed from pond C instead of one mixed sample

ACCOMPANYING ANALYSIS FOR POND STUDY

4.5 Test: Content of 4.4'-diphenylmethanediamine in fish samples

Sample preparation

method No.: 2011-0322301-92D HPLC method No.: K 2011-0322501-92D

Laboratory manager: Dr. Jaeger

Day	Date	Pond / Fish	mg/kg	
112	02.09.92	A/1,2,3,4,5,6	n.d. <1	
112	02.09.92	B/1,3,4,5,6	n.d. <1	
112	02.09.92	C/1,2,4	n.d. <1	
n.d. :	Not detecta	ble, recovery rates (s	ee section 3.2) not tak	en into account

4.6 Test: Content of 4,4'-diphenylmethane-N,N'-dibutyl-urea in fish samples

Sample preparation

method No.: 2011-0322401-92D HPLC method No.: K 2011-0322601-92D

Laboratory manager: Dr. Jaeger

Day	Date	Pond / Fish	mg/kg	
112	02.09.92	A/1,2,3,4,5,6	n.d. <1	
112	02.09.92	B/1,3,4,5,6	a.d. <1	
112	02.09.92	C/1,2,4	n.d. <1	
n.d. :	Not detecta	ble, recovery rates (s	ee section 3.2) not taken into acc	count

ACCOMPANYING ANALYSIS FOR POND STUDY

5. Notes

5.1 Weighing of sesiment samples

The sediment samples were weighed after the water covering them had been decanted off (the samples were supplied in glass containers with residual water). This procedure was observed in the preparation of all samples.

5.2 Inhomogeneity of samples

The samples of pond sediment contained solid particles of polymerized diphenylmethane diisocyanate (MDI) in a wide variety of sizes. The following samples were observed to be inhomogeneous:

Pond C	20.05.92
Pond C	27.05.92
Pond C	10.06.92
Pond C	08.07.92
Pond C	02.09.92

5.3 Determination of diphenylmethanediamine (MDA) in pond sediment

During determination of MDA in pond sediment, analytical method 2011-0322201-92D had to be supplemented by an additional clean-up step to separate the large incidental quantities of MDI which were present after the sediment had been extracted. The ether extract was shaken out with 50 ml of 1 mol HCl three times, adjusted to alkaline and re-extracted with 50 ml of ether three times. Thereafter the sample extract was prepared in accordance with analytical procedure 2011-0322201-92D (see section 4.3). The supplemented procedure was used for the following samples:

Pond C	20.05.92
Pond C	27.05.92
Pond C	10.06.92
Pond C	08.07.92
Pond C	02.09.92

ACCOMPANYING ANALYSIS FOR POND STUDY

5.4 Quantification of MDA and MDI derivative by HPLC

The results stated here were also confirmed by standard addition of 0.5-1 mg/l to the final chromatography solutions in which no MDA or MDI was detected within the limit of detection of 0.5 mg/l.

5.5 Documentation of the final results for 4.4'-diphenylmethane diisocynate (MDI)

The ratio between the molar masses of pure MDI (250.26) and 4,4'-diphenyl-methane-N,N'-dibutylurea (580.75) is 1:2.32. The corresponding conversion factor 0.43 was multiplied with the concentration of MDI urea derivative to give the content of pure MDI. The content of 4,4'-diphenylmethane diisocyanate (MDI) in the various samples as determined by HPLC is shown below.

5.6 Table of results for 4.4'-MDI

Day	Date	Pond water		
•		Pond B mg/l	Pond C mg/l	
0	13.05.92	n.d. < 0.0054	n.d. < 0.0054	
1	14.05.92	n.d. < 0.0054	n.d. < 0.0054	
7	20.05.92	n.d. < 0.0054	0.0077	
14	27.05.92	n.d. < 0.0043	0.0229	
28	10.06.92	n.d. < 0.0043	n.d. < 0.0043	
56	08.07.92	n.d. < 0.0043	n.d. < 0.0043	
112	02.09.92	n.d. < 0.0043	n.d. < 0.0043	

n.d. = not detectable

<... = detection limit

ACCOMPANYING ANALYSIS FOR POND STUDY

Continuation of table of results for 4,4'-MDI

Day	Date		Pond sedime	nt		Fish
i i		Pond	i B	Pon	d C	
		mg/l	kg .	mg/	kg	mg/kg
-1	12.05.92	I	n.d. < 0.215	I	n.d. < 0.215	•
		II	n.d. < 0.215	П	n.d. < 0.215	
7	20.05.92	I	10.836	I	8966	
		II	1.376	II	7726	•
14	27.05.92	I	0.387	1	14590	
		II	4.816		12267	
				3	8549	•
				2 3 4 5	4315	*
				5	17659	
				6	409	
28	10.06.92	I	1.118	I	3380	
		П	1.161	II	3388	•
56	08.07.92	I	1.376	п	1359	
		II	0.559	II	2188	•
112	02.09.92	I	n.d. < 0.215	I	0.559	A/1,2,3,4,5,6 n.d. < 0.43
		II	0.903	II	0.774	B/1,3,4,5,6 n.d. < 0.43 C/1,2,4 n.d. < 0.43
n.d.	= not dete	ctable				
<	= detection	n limit				

6. **Evaluation and comments**

The raw data have been checard and will be archived.

ACCOMPANYING ANALYSIS FOR POND STUDY

7. Declaration by study director

This study was carried out in accordance with the OECD Principles of Good Laboratory Practice (GLP) of 04.02.83 (published in the Federal Gazette No. 42a of 02.03.83) and the Principles of Good Laboratory Practice (GLP) set out in Appendix 1 of the German legislation governing protection against hazardous substances (Chemicals Act) of 14.03.90 (published in the Federal Gazette, Part I of 22.03.90).

8. Archiving of records

GLP-Archiv, Bayer AG, Central Analysis Department, ZF-DZA Analytik Leverkusen/OAL, Gebäude O 13, 51368 Leverkusen

Study plan, raw data sheets, chromatograms, spectra, other documents needed for verification, final and inspection reports.

Appendix: Declaration by Quality Assurance Unit (QAU)

Study director:

08.02.93

(signed) K. Jaeger

(Date)

Deputy (Dr. Fus):

(08.02.93

(signed) M. Fus

(Date)

Distribution:

Dr. Klebert, LS-P/AD DOR, Gebäude A 608

Archive

Head of test facility

QS/ZF-DZA Koordination Alt- und Neustoffanalytik

Dr. Keller Dr. Jaeger

D.I. Sporenberg

Dr. Heimbach, PF-F/UF-OE, MON, Gebäude 6620

Quality Assurance declaration for final report

Study No./Commission No. : G 92/0061/01 LEV Title of GLP study : Polymeric MDI

Type of study: Accompanying analysis for pond study

This GLP study was monitored continuously by Quality Assurance. The dates of the inspections and the dates on which reports to the head of the test facility and the study director were written are listed below.

(Date)	(Date)
May 12, 1992	'May 12, 1992
January 29, 1993	January 29, 1993
February 8, 1993	February 8, 1993

The results stated in the final report on this study have been examined on the basis of the current SOPs/analytical methods. To the best of our knowledge they correspond to the available raw data.

Quality Assurance

February 8, 1993 (signed) W. Willers

(Date) (Willers)

BAYER AG ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993

Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr.Jaeger Vertreter : Dr.Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608 Au

Auftragsnummer: --

Chemische Bezeichnung : --

Summenformel : -- Molare Masse : -- g/mol

CAS-Nr. : -- Charge/Partie-Nr. : 2014

Proben-Nr./Jahr : 432732/1992 Datum Probennahme : 01.04.92

Herstellbetrieb : PU-P/UER 2 Herstelldatum : 01.04.92

Produkt-Nr. : 410 012 01 Haltbarkeit bis : 01.10.92

Beginn der Prüfung : 13.05.92 Ende der Prüfung : 13.01.93

1. Zielsetzung der Studie

Im Rahmen der vom International Isocyanat Institute (III) veranlassten Studie 101-EU-ENV soll eine Transport Havarie simuliert werden, bei der 4,4'-Diphenylmethandiisocyanat (MDI) in ein aquatisches Ökosystem gelangt. Dieses aquatische Ökosystem wird in einer aus drei Teichen bestehenden Modellteichanlage simuliert, eine genaue Versuchsbeschreibung findet sich im Prüfplan mit der Studien-Nr. E 413 0629-5 (Versuchsbetreuer Dr.Heimbach PF-F/UF-OE). Die Dosierung der Teiche ist nachfolgend aufgeführt:

Teich A: Kontrolle

Teich B: 1 g MDI/1 Teichwasser
Teich C: 10g MDI/1 Teichwasser

Häufigkeit der Verabreichung: einmal

Die von ZF-DZA/OAL (Labors Dr.Jaeger und Dr.Fus) unter der Studien-Nr. G 92/0061/01 LEV durchgeführte Begleitanalytik zur Teichstudie umfasst die Analyse der Probenmatrizes Wasser, Fisch und Sediment in Bezug auf monomeres MDI (4,4'-Diphenylmethandiisocyanat) und MDA (4,4'-Diphenylmethandiamin):

Probena	nmetermine	Probenart
Tag -1	12.Mai 1992	Sediment
Tag 0	13.Mai 1992	Wasser
Tag 1	14.Mai 1992	Wasser
Tag 7	20.Mai 1992	Wasser, Sediment
Tag 14	27.Mai 1992	Wasser, Sediment
Tag 28	10.Juni 1992	Wasser, Sediment
Tag 56	08.Juli 1992	Wasser, Sediment
Tag 112		992 Wasser, Sediment, Fisch

BAYER AG ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993

Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr.Jaeger Vertreter : Dr.Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Auftragsnummer: --

Die Sedimentproben sind im Regelfall Mischproben aus sechs Einzelproben, wobei die Positionen der Probenahmen in der Studie E 413 0629-5 genau beschrieben werden. Im Projektvorschlag für das International Isocyanate Institute wurde folgende anzustrebende Nachweisgrenzen für MDA und MDI festgelegt:

Wasser: Sediment: 0,1 mg/l 1 mg/kg

Fisch:

1 mg/kg

2. Charakterisierung der Testsubstanz

Unter der Studien-Nr. G 92/0061/00 LEV (Prüfleiter Dr.Fus) wurde eine analytische Stoffbilanz der Prüfsubstanz MDI-Polymer (Charge/Partie-Nr. 2014, Proben-Nr. 432732/1992) durchgeführt.

Kurze Beschreibung der Analysenmethoden

3.1 Extraktion und Anreicherung von MDA und MDI aus wässrigen Lösungen (Analysenmethode 2011-0326201-92D)

In der wässrigen Probe wird das MDI entweder mit Dibutylamin zu 4,4'-Diphenylmethan-N,N'-dibutylharnstoff (HPLC-Bestimmung) oder mit N-4-Nitrobenzylpropylamin (DC-Bestimmung) zum entsprechenden Harnstoff derivatisiert. 4,4'-Diphenylmethandiamin und das Harnstoffderivat werden nachfolgend mit Toluol extrahiert sowie der Extrakt am Rotationsverdampfer aufkonzentriert. Die mit N-4-Nitrobenzylpropylamin derivatisierte, aufkonzentrierte Chromatographielösung kann dann direkt einer DC (-Dünnschichtch: matographie) Bestimmung zugeführt werden. Bei Derivatisierung mit Dibutylamin erfolgt eine Quantifizierung per HPLC (Hochdruckflüssigkeitschromatographie). Eine Kontrolle über die Wiederfindung an MDI ist erst ab der organischen Toluol-Phase möglich, da MDI im wässrigen Medium sofort als Harnstoff ausfällt. Unter dieser Veraussetzung liegt die mittlere Wiederfindungsrate bei der DC-Bestimmung für MDI bei 90%, auch für MDA findet sich eine mittlere Wiederfindungsrate von 90%.

BAYER AG ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993 Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr. Jaeger Vertreter : Dr. Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608 Auftragsnummer: --

3.2 Extraktion und Anreicherung von MPA und MDI aus Forellen (Analysenmethoden 2011-0322401-92D und 2011-0322301-92D)

Die getöteten und eingefrorenen Forellen werden homogenisiert, die Zielkomponente MDI mit Dibutylamin zu 4,4'-Diphenylmethan-N,N'-dibutylharnstoff derivatisiert und mittels Toluol extrahiert. Der Toluolextrakt wird unter Zugabe von Methanol aufkonzentriert und durch HPLC analysiert. Bei der MDA Bestimmung wird das Fischhomogenat mit Diethylether extrahiert, sowie das Aufkonzentrat ebenfalls mit HPLC untersucht. Bei Erstellung der Analysenmethoden 2011-0322401-92D und 2011-0322301-92D betrug die mittlere Wiederfindungsrate an MDA 69%, die von MDI 84%, wobei das MDI zum Extrakt des Fischhomogenats dotiert wurde.

3.3 Extraktion und Anreicherung von MDA und MDI aus Teichsediment (Analysenmethoden 2011-0322101-92D und 2011-0322201-92D)

Nach Homogenisierung des Teichsediments mit Natriumsulfat wird das darin nachzuweisende MDI mit Dibutylamin zu 4,4'-Diphenylmethan-N,N'-dibutylharnstoff derivatisiert. Danach wird mit Toluol extrahiert, der Toluolextrakt aufkonzentriert und die Analyse mit HPLC durchgeführt. Bei der MDA Bestimmung verfährt man analog, in Abänderung wird mit Diethylether als Extraktionsmittel gearbeitet. Zur Bestimmung der Wiederfindungsraten bei Erstellen der Analysenmethoden wurde Sediment mit MDA bzw. der Toluolextrakt mit MDI dotiert. Die mittleren Wiederfindungsraten lagen für MDI bei 82%, die für MDA bei 56%.

3.4 <u>Gehaltsbestimmung von MDA in den unter 3.1 - 3.3 gewonnenen Extrakten</u> <u>per HPLC (Analysenmethode K 2011-0322501-92D)</u>

Prufung:

Gehalt an MDA in Probenextrakten aus Fisch, Sediment

und Wasser

Methoden-Nr.:

K 2011-0322501-92D

Kurzbeschreibung: HPLC-Methode

isokratisch

Laufmittel

300ml Acetonitril, 700ml dest. Wasser

2ml o-Phosphorsaure

Trennsaule

Cyclobond I (b-Cyclodextrin, Astec Cat.-No.41010) Länge 250mm, innerer Durchmesser-4,6mm, Fluß etwa lml/min

UV-Detektion bei 220nm

Auswertung nach der Methode des externen

Standards

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Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993 Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr.Jaeger Vertreter : Dr. Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608 Auftragsnummer: --

3.5 Gehaltsbestimmung von MDI in den unter 3.1 - 3.3 gewonnenen Extrakten per HPLC (Analysenmethode K 2011-0322601-92D)

Prufung:

Gehalt an MDI in Form des Derivates 4,4'-Diphenyl-

methan-N, N'-dibutylharnstoff

Methoden-Nr.:

K 2011-0322601-92D

Kurzbeschreibung: HPLC-Methode

Gradientenelution

La mittel A: 300ml Acetonitril, 700ml dest. Wasser

2ml o-Phosphorsäure

B: 1000ml Acetonitril, 2ml o-Phosphorsäure

Trennsäule

RP8 Fertigsäule (Merck Cat. 50341) Länge 250mm, innerer Durchmesser -4,6mmm, Fluß (t-0 min)-lml/min Zeitprogrammierte UV-Detektion im

Bereich 220-250nm

Auswertung nach der Methode des externen

Standards

3.6 Angaben zur Linearität und Präzision der HPLC-Bestimmungen von MDI und MDA

Die Linearität des Meßverfahrens für MDI und MDA nach obigen Analysenmethoden (3.4 - 3.5) wurde im Bereich 0,5-10mg/l bezogen auf die Meßlösung anhand von sechs Meßpunkten überprüft und verifiziert. Bei der Quantifizierung der angereicherten Probenextrakte wird ein Kalibrierpunkt bei 10mg/l Meßlösung gesetzt und nach der Methode des externen Standards ausgewertet. Zur Ermittlung der Präzision des Meßverfahrens wurden sechs unabhängige analytische Bestimmungen von 2mg/l haltigen Meßlösungen durchgeführt.

MDA	MDI-Derivat	
1,99mg/1	2,01mg/1	Arithmetischer Mittelwert
0,10mg/1	0,04mg/1	Standardabweichung
0,36mg/1	0,15mg/1	Spannbreite
0,11mg/1	0,04mm/1	Ergebnisunsicherheit
1, 7 +/- 0,11mg/1	2.01 /- 0.04mg/1	Vertrauensbereich

Die Nachweisgrenzen der HPLC Bestimmung liegen bezogen auf die Meßlösung bei jeweils 0,5mg/l für MDA und MDI-Derivat.

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: 05.Feb.1993 Datum Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr. Jaeger Vertreter : Dr. Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Auftrag: nummer: --

3.7 Gehaltsbestimmung von MDI und MDA aus den wässrigen Lösungen (s.3.1) per Dünnschichtchromatographie (Analysenmethode 2011-0326301-92D)

Zwecks Absicherung und Ergänzung zur HPLC-Quantifizierung wurde der Gehalt an MDI und MDA in den Extrakten der Wasserproben (3.1) auch mittels Dünnschichtchromatographie bestimmt. Grundlage des Verfahrens ist die Umsetzung der Probelösung mit 4-Nitrobenzylpropylamin, wobei das MDI zum Harnstoffderivat umgesetzt wird und das MDA weiterhin underivatisiert vorliegt. Die Umsetzung verhindert das weitere Abreagieren des Isocyanats mit dem Wasser und erlaubt die Umwandlung der Nitroverbindung in einen Farbstoff zur Visualisierung per Dünnschichtchromatographie. Die visuelle Auswertung erfolgt nach Reduktion, Diazotierung und Kupplung des Harnstoffderivates bzw. von MDA auf der DC-Platte zu den entsprechenden Azofarbstoffen nach der Methode des externen Standards.

MDA und MDI-Derivat werden durch ihre unterschiedlichen RF-Werte und ihre unterschiedliche Farbe auf der Platte nebeneinander bestimmt.

Prufung: Gehalt an MDA und MDI Probenextrakten aus Wasser

Methoden-Nr: 2011-0326301-92D Trennkammer: Flachbodenkammer Schicht: Kieselgel 60 F 254

Schichtdicke: 0,25mm

Fließ, 'ttel: Aceton/Toluol-4ml/6ml

Auftragevolumen: je 10µl der Meßlösung, Trennstrecke etwa 7cm,

Trennzeit etwa 30 min

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Prufleiter : Dr. Jaeger Vertreter : Dr. Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608 Auft

Auftragsnummer: --

4. Ergebnisse

4.1 Prüfung: 4.4'-Diphenylmethandiamin Gehalt in den

Wasserproben

Probenvorcereitung

Methoden-Nr.:

2011-0326201-92D

DC

Methoden-Nr.:

2011-0326301-92D

Laborleiter:

Dr. Fus

HPLC

Methoden-Nr.:

K 2011-0322501-92D

Laborleiter:

Dr.Jaeger

		HPLC		DC	
Tag	Datum	Teich B mg/l	Teich C mg/l	Teich B mg/l	Teich C mg/l
0	13.05.92	n.n.<0,0125	n.n.<0,0125	n.n.<0.0125	n.n.<0,0125
1	14.05.92	n.n.<0,0125	n.n.<0,0125	n.n.<0,0125	n.n.<0.0125
7	20.05.92	n.n.<0,0125	n.n.<0,0125	n.n.<0,0125	n.n.<0,0125
14	27.05.92	n.n.<0,01	n.n.<0,01	n.n.<0,01	n.n.<0,01
28	10.06.92	n.n.<0,01	n.n.<0,01	n.n.<0,01	n.n.<0,01
56	08.07.92	n.n.<0,01	n.n.<0,01	n.n.<0,01	n.n.<0,01
112	02.09.92	n.n.<0,01	n.n.<0,01	n.n.<0,01	n.n.<0,01

n.n. = nicht nachweisbar, Wiederfindungsrate (s.3.1) nicht berücksichtigt

Die angegebenen Nachweisgrenzen variieren in Abhängigkeit vom aufkonzentrierten Probevolumen. Bei Tag 0, 1 und 7 wurden 200ml Wasser aufgearbeitet, an den restlichen Tagen waren es 250ml Probevolumen.

BAYER AG ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1

: 05.Feb.1993 Datum

Studiennummer: G 92/0061/01 LEV

Prufleite : Dr.Jaeger : Dr. Theimer Vertreter

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Auftragsnummer: --

4.2 Prufung: 4.4'-Diphenylmethan-N.N'-dibutylharnstoff

Gehalt in den Wasserproben Probenvorbereitung

Methoden-Nr .:

Methoden-Nr.:

Laborleiter:

HPLC

Methoden-Nr.: Laborleiter:

2011-0326201-92D

2011-0326301-92D

Dr. Fus

K 2011-0322601-92D

Dr.Jaeger

		HPLC		DC		
Tag	Datum	Teich B mg/l	Teich C mg/l	Teich B mg/l	Teich C mg/l	
0	13.05.92	n.n.<0,0125	n.n.<0,0125	n.n.<0.025	n.n.<0,025	
1	14.05.92	n.n.<0,0125	n.n.<0,0125	n.n.<0,025	n.n.<0.025	
7	20.05.92	n.n.<0,0125	0,0178	n.n.<0,025	n.n.<0,025	
14	27.05.92	n.n.<0,01	0,0533	n.n.<0,02	n.n.<0,02	
28	10.06.92	n.n.<0,01	n.n.<0,01	n.n.<0,02	n.n.<0,02	
56	08.07.92	n.n.<0,01	n.n.<0,01	n.n.<0,02	n.n.<0,02	
112	02.09.92	n.n.<0,01	n.n.<0,01	n.n <0,02	n.n.<0,02	

n.n. = nicht nachweisbar, Wiederfindungsrate (s.3.1) nicht berücksichtigt

Die angegebenen Nachweisgrenzen variieren in Abhängigkeit vom aufkonzentrierten Probevolumen. Bei Tag 0, 1 und 7 wurden 200ml Wasser aufgearbeitet, an den restlichen Tagen waren es 250ml Probevolumen.

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ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993

Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr. Jaeger Vertreter : Dr. Theimer

Prufsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Auftragsnummer: --

4.3 Prüfung:

4.4'-Diphenylmethandiamin Gehalt im Teichsediment

Probenvorbereitung

Methoden-Nr.:

HPLC

Methoden-Nr.: Laborleiter: 2011-0322201-92D

K 2011-0322501-92D

Dr. Jaeger

Tag	Datum	rum Teich B mg/kg		Teich C mg/kg	
-1	12.05.92	I	n.n.<0,5	I	n.n.<0,5
		II	n.n.<0,5	II	n.n.<0,5
7	20.05.92	I	12,8	I	8,1
		II	n.n.<0,5	II	33,9
14	27.05.92	I*	n.n.<0,5	I**	n.n.<0,5
		II*	n.n.<0,5	II**	n.n.<0,5
28	10.06.92	I	n.n.<0,5	I	1.6
		II	n.n.<0,5	II	n.n.<0,5
56	08.07.92	I	n.n.<0,5	I	n.n.<0,5
		II	n.n.<0,5	II	2,1
112	02.09.92	I	n.n.<0,5	I	n.n.<0,5
		II	n.n.<0,5	II	n.n.<0,5

I, II: Probenbezeichnung, alle Gehaltsbestimmungen per HPLC

* : Die Sedimentproben der Positionen 1-6 im Modellteich B wurden

getremat angeliefert und zu einer Mischprobe vereinigt

I** : Sedimentprobe aus Position 1 des Modellteichs C
II** : Sedimentprobe aus Position 3 des Modellteichs

n.n.: nicht nachweisbar, Wiederfindungsraten (s.3.3) nicht

berücksichtigt

BAYER AG ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993

Studiennummer: G 92/0061/01 LEV

Prufleiter : Dr.Jaeger Vertreter : Dr. Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Auftragsnummer: --

4.4 Prufung: 4.4'-Diphenylmethan-N.N'-dibutylharnstoff

Gehalt im Teichsediment

Probenvorbereitung

Methoden Nr .:

Methoden-Nr.:

Laborleiter:

2011-0322101-92D

K 2011-0322601-92D

Dr.Jaeger

Tag	Datum	Tei mg/	ch B kg	Tei	ch C kg
-1	12.05.92	I	n.n.<0,5	I	n.n.<0,5
		II	n.n.<0,5	II	n.n.<0,5
7	20.05.92	I	25,2	I	20852
		II	3,2	II	17968
14*	27.05.92	I	0,9	1	33931
		II	11,2	1 2 3	28529
				3	19883
				5	10034
				5	41069
				6	951
28	10.06.92	I	2,6	I	7860
		II	2,7	II	7878
56	08.07.92	I	3,2	I	3161
		II	1,3	II	5089
112	02.09.92	I	n.n.<0,5	I	1,3
		II	2,1	II	1,8

n.n.: nicht nachweisbar, Wiederfindungsraten (s.3.3) nicht berücksichtigt

I, II: Probenbezeichnung, alle Gehaltsbestimmungen per HPLC

: bei Tag 14 wurde bei Teich C keine Mischprobe sondern sechs Einzelproben bestimmt

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ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1

: 05.Feb.1993 Datum

Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr.Jaeger : Dr. Theimer Vertreter

Prufsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Auftragsnummer: --

4.5 Prufung:

4.4'-Diphenylmethandiamin Gehalt in Fischproben

Probenvorbereitung

Methoden-Nr.: HPLC

Methoden-Nr.: Laborleiter:

2011-0322301-92D

K 2011-0322501-92D

Dr.Jaeger

Tag	Datum	Teich / Fische	mg/kg
112	02.09.92	A / 1,2,3,4,5,6	n.n. <1
112	02.09.92	B / 1,3,4,5,6	n.n. <1
112	02.09.92	C / 1,2,4	n.n. <1

n.n : nicht nachweisbar, Wiederfindungsraten (s.3.2) nicht

berücksichtigt

alle Gehaltsbestimmungen per HPLC

4.6 Prufung: 4.4'-Diphenylmethan-N.N'-dibutylharnstoff

Gehalt in Fischproben

Probenvorbereitung

Methoden-Nr.:

HPLC

Methoden-Nr.: Laborleiter:

2011-0322401-92D

K 2011-0322601-92D

Dr.Jaeger

Tag	Datum	Teich / Fische	mg/kg
112	02.09.92	A / 1,2,3,4,5,6	n.n. <1
112	02.09.92	B / 1,3,4,5,6	n.n. <1
112	02.09.92	C / 1,2,4	n.n. <1

n.n : nicht nachweisbar, Wiederfindungsraten (s.3.2) nicht berücksichtigt

alle Gehaltsbestimmungen per HPLC

BAYER AG ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993 Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr. Jaeger Vertreter : Dr. Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608 Auftragsnummer: --

5. Anmerkungen

5.1 Einwaage der Sedimentproben

Die Sedimentproben wurden nach Abdekantieren des überstehenden Wassers (die Proben wurden im Glasgefäß mit Restmengen an Wasser angeliefert) eingewogen. Diese Vorgehensweise wurde bei allen Probenvorbereitungen beibehalten.

5.2 Probeninhomogenitäten

Die Proben des Teichsedimentes enthielten Feststoffanteile von polymerisiertem Methandiphenyldiisocyant (MDI) unterschiedlichster Größen. Diese Probeninhomogenität wurde bei folgenden Proben beobachtet:

Teich C 20.05.92

Teich C 27.05.92

Teich C 10.06.92

Teich C 08.67.92

Teich C 02.09.92

5.3 Bestimmung von Methandiphenyldiamin (MDA) im Teichsediment

In Ergänzung zur Analysenmethode 2011-0322201-92D mußte bei der Bestimmung von MDA im Teichsediment ein zusätzlicher Clean-Up Schritt zur Abtrennung der hohen Begleitmengen an MDI nach der Extraktion des Sedimentes aufgenommen werden. Dabei wird der Etherextrakt 3 mal mit je 50ml 1 molarer HCl ausgeschüttelt, alkalisch gestellt und 3 mal mit jeweils 50ml Ether reextrahiert. Die weitere Aufarbeitung des Probenextraktes erfolgte wie in der Analysenvorschrift 2011-0322201-92D beschrieben. Dieses Verfahren wurde bei folgenden Proben angewendet:

Teich C 20.05.92

Teich C 27.05.92

Teich C 10.06.92

Teich C 08.07.92

Teich C 02.09.92

BAYER AG ZF-D Zentrale Analytik

Gebäude O 13 5090 Leverkusen 1 Datum : 05.Feb.1993

Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr. Jaeger Vertreter : Dr. Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608 Auftragsnummer: --

5.4 Quantifizierung von MDA und MDI-Derivat per HPLC

Die angegebenen Ergebnisse wurden durch Standardadditionen zur Endkonzentration der Meßlösung von 0,5 - lmg/l zusätzlich abgesichert, dies gilt für die Meßlösungen in denen innerhalb der Nachweisgrenze von 0,5mg/l kein MDA und MDI nachweisbar war.

5.5 Angabe des Endergebnisses für 4.4'-Diphenylmethandiisocyanat (MDI)

Die molaren Massen von reinem MDI (250,26) und 4,4'-Diphenylmethan-N,N'-dibutylharnstoff (580,75) verhalten sich wie 1: 2,32. Der hizraus resultierende Umrechnungsfaktor von 0,43 ist mit der Konzentrationsangabe für das MDI-Harnstoffderivat zu multiplizieren, um auf den Gehalt an reinem MDI zu schließen. Nachfolgend sind die Gehaltsangaben der HPLC-Bestimmungen für 4,4'-Diphenylmethandiisocyanat (MDI) in den unterschiedlichen Proben aufgeführt:

5.6 Ergebnistabellen für 4.4'-Diphenvlmethandiisocyanat

Tag	Datum	Teichwasse	ser
		Teich B mg/l	Teich C mg/l
0	13.05.92	n.n.<0,0054	n.n.<0,0054
1	14.05.92	n.n.<0,0054	n.n.<0,0054
7	92. ز 20. 20	n.n.<0,0054	0,0077
14	27.05.92	n.n.<0,0043	0,0229
28	10.06.92	n.n.<0,0043	n.n.<0,0043
56	08.07.92	n.n.<0,0043	n.n.<0,0043
112	02.09.92	n.n.<0,0043	n.n.<0,0043

BAYER AG

ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1

Datum : 05.Feb.1993

Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr.Jaeger Vertreter : Dr.Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr. M ebert, LS-P/AD DOR, Gebäude A 608 Auftragsnummer: --

Fortsetzung der Ergebnistabelle:

Tag	Datum	Teichsedime	ent Teich C	Fisch
		mg/kg	mg/kg	mg/kg
-1	12.05.92	I n.n.<0,21	15 I n.n.<0,215	
		II n.n.<0,2	15 II n.n.<0,215	
7	20.05.92	I 10,836	1 8966	
		II 1,376	II 7726	
14	27.05.92	I 0,387	1 14590	
		II 4,816	2 12267	
		2000 2000	3 8549	
			4 4315	
			4 4315 5 17659 6 409	
			6 409	
28	10.06.92	I 1,118	I 3380	
		II 1,161	II 3388	
56	08.07.92	I 1,376	I 1359	
		II 0,559	II 2188	
112	02.09.92	I n.n.<0,2	15 I 0,559	A/1,2,3,4,5,6 n.n.<0,43
		II 0,90		B/1,3,4,5,6 n.n.<0,43 C/1,2,4 n.n.<0,43

BAYER AG ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1 Datum : 05.Feb.1993

Studiennummer: G 92/0061/01 LEV Prüfleiter : Dr.Jaeger Vertreter : Dr.Theimer

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608 Auftragsnummer: --

6. Bewertung und Kommentar

- Rohdaten sind überprüft und werden archiviert

Erklärung des Prüfleiters

Die Untersuchungen wurden in Übereinstimmung mit den OECD-Grundsätzen der Guten Laborpraxis (GLP) vom 04.02.83 (veröffentlicht im Bundesanzeiger Nr.42a vom 02.03.83) und den Grundsätzen der Guten Laborpraxis (GLP) gemäß Anhang 1 des Gesetzes zum Schutz vor gefährlichen Stoffen (Chemikaliengesetz) vom 14.03.1990 (veröffentlicht im Bundesgesetzblatt, Teil I vom 22.03.1990) durchgeführt.

8. Archivierung von Aufzeichnungen

GLP-Archiv, Bayer AG, ZF-DZA Analytik Leverkusen/OAL, Gebäude O 13, 5090 Leverkusen 1

Prüfplan, Rohdatenblätter, Chromatogramme, Spektren, weitere für eine Nachprüfung relevante Unterlagen, Abschluß- und Inspektionsberichte.

Anlagen: Erklärung der Qualitätssicherungseinheit (QS)

BAYER AG

ZF-D Zentrale Analytik

Gebäude 0 13 5090 Leverkusen 1

: 05.Feb.1993 Datum

Studiennummer: G 92/0061/01 LEV

Prüfleiter : Dr.Jaeger : Dr. Theimer Vertreter

Prüfsubstanz: MDI-Polymer

Auftraggeber: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Auftragsnummer: --

Prüfleiter:

Betreuer:

(Dr.Fus)

Verteiler: Dr.Klebert, LS-P/AD DOR, Gebäude A 608

Archiv

Leiter Prüfeinrichtung

QS/ZF-DZA Koordination Alt- und Neustoffanalytik

Dr.Keller Dr. Jaeger

D. I. Sporenberg

Dr. Heimbach, PF-F/UF-OE, MON, Gebäude 6620

Qualitätssicherungserklärung zum Abschlußbericht

Studien-Nr. bzw. Auftrag-Nr.: G 92/0061/04 LEV

Titel der GLP-Untersuchung : MDI-Polymer

Art der studie: Begleitaualytik lür Teichstüdic

Diese GLP-Untersuchung wurde laufend durch die Qualitätssicherung überprüft. Die Zeitpunkte der Inspektionen und die Zeitpunkte der Berichte an den Leiter der Prüfeinrichtung und an den Prüfleiter sind nachfolgend aufgeführt:

<u>Überprüfung</u> (Datum)	<u>Bericht</u> (Datum)
17.5.92	12.5.92
29.1.97	29.1.93
8.2.93	8.2.93

Die im Abschlußbericht dieser Untersuchung wiedergegebenen Ergebnisse werden auf der Basis der aktuellen SOP, 's/Analysenmethoden überprüft. Sie entsprechen nach unserem besten Wissen den vorliegenden Rohdaten.

Qualitätssicherung:

8. 2. 93

(Datum)

(WILLERS)

CERTIFICATE OF AUTHENTICITY

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